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JOURNAL

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ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

PART II.

General and Physical Chemistry.

Influence of Ultra-red Characteristic Frequencies on the Coefficient of Refractivity in the Visible Portions of the Spectrum. J. WIMMER (*Physikal. Zeitsch.*, 1918, **19**, 483—486).—A mathematical paper, in which it is shown that the relationship, which may be deduced from the Drude theory and the work of Dehlinger, may be used to calculate the influence of the ultra-red characteristic frequencies on the refractive index in the visible region. Further, the relationship gives a picture of the nature of the vibrations to which the characteristic frequencies are due. Corresponding with the k relationship for solids with two atoms or atomic groups in the molecule, a similar k relationship may be deduced by analogous methods for liquid substances with three atomic groups as origin of the ultra-red characteristic frequencies. In the case of monohydric alcohols, it is shown that in the ultra-red absorption spectrum the wave-lengths of the superposed harmonic absorption region are related as the roots of the masses of the vibrating atomic groups. J. F. S.

Origin of Spectra. J. C. MCLENNAN (*Proc. Physical Soc., London*, 1918, **31**, 1—29).—The Guthrie lecture, in which the modern views of spectroscopy are discussed along with the methods of determination of spectra in the extreme ultra-violet. J. F. S.

Fundamental Frequencies in the Spectra of Various Elements. J. C. MCLENNAN and H. J. C. IRETON (*Phil. Mag.*, 1918, [vi], **36**, 461—471).—It is shown that when zinc and cad-

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mium vapours respectively are bombarded by electrons the kinetic energy of which is gradually increased, monochromatic radiation is suddenly emitted by the vapour when the impact voltage is that given by the quantum relation for the frequency $\nu=(1\cdot5,S)-(2p_2)$. When the impact voltage is increased beyond this amount, no additional radiation is observed until that corresponding with the frequency $\nu=(1\cdot5,S)-(2,P)$ is applied. When these conditions are realised, the wave-lengths, the frequencies of which are given by $\nu=(1\cdot5,S)-(2p_3)$ and $\nu=(1\cdot5,S)-(2,P)$, are then recorded on the plates. It is also shown that when a bunsen flame is fed with the vapour of zinc, it is possible to obtain monochromatic radiation of wave-length $\lambda=3075\cdot99$ Å.U. The evidence adduced, to show that the series of wave-lengths given by $\nu=(1\cdot5,S)-(m,P)$, is probably fundamental from the point of view of electronic vibrations within the atoms of the elements mercury, zinc, cadmium, magnesium, calcium, and probably strontium and barium. J. F. S.

Ultra-violet Spectra of Magnesium and Selenium. J. C. McLennan and J. F. T. Young (*Phil. Mag.*, 1918, [vi], **36**, 450—460).—The spectra of magnesium for (*a*) the spark in air, (*b*) the arc in air, and (*c*) the arc in a vacuum have been investigated in the region $\lambda=2852\cdot22$ Å.U.—$\lambda=2000$ Å.U., and some fifty-eight new lines have been observed. The existence of the line $\lambda=2026$ Å.U., first mentioned by Saunders, has been confirmed, and considerations are brought forward supporting the view that the series $\nu=(1\cdot5,S)-(m,p_2)$ has a real existence. Twelve new lines are recorded in the selenium spark spectrum between $\lambda=2200$ Å.U. and $\lambda=1850$ Å.U. Five lines in the selenium arc have been found in the same region. In the sources used no part of the spectrum longer in wave-length than $\lambda=2200$ Å.U. was present. The adsorption spectrum of selenium metal in the carbon arc has been investigated and a reversal found at $\lambda=1960$ Å.U., which is the strongest line in both the spark and arc spectrum. If the absorption of selenium vapour should prove to be analogous to that of mercury, zinc, and cadmium, this would indicate that the two series $\nu=(1\cdot5,S)-(m,P)$ and $\nu=(1\cdot5,S)-(m,p_2)$ for selenium are in the extreme ultra-violet. J. F. S.

Measurement of the Short Wave-length Portion of the Cerium Arc Spectrum in Terms of the International Normal. Philipp Klein (*Zeitsch. wiss. Photochem.*, 1918, **18**, 45—83).—The short wave-length spectrum of cerium has been measured by means of a concave Rowland grating, 6·5 metres in diameter and ruled with 20,000 lines per inch. Cerium nitrate was vaporised in carbon, iron, and copper arcs for the purpose, and the spectra photographed. Long lists of the lines measured are given, and these are compared with the previous measurements of Exner and of Haschek and Bakowski. An accuracy of measurement of 0·003 Ångstrom unit is claimed over the range 2518·509 $\mu\mu$—4546·066 $\mu\mu$, this being the range investigated. The measurements were made

with the second order spectrum. The intensity of the lines is indicated, as also is the presence of doublets, reversed lines, and broadened lines. J. F. S.

The Arc Spectrum of Zirconium, Measured in Terms of the International Normal. W. VAHLE (*Zeitsch. wiss. Photochem.*, 1918, **18**, 84—137).—The arc spectrum of zirconium has been measured by means of a concave Rowland grating 6·34 metres in diameter and ruled with 787 lines per mm. Zirconium nitrate was vaporised in a carbon arc and the spectrum photographed. Long lists of the lines measured are given over the range 2285·229 $\mu\mu$—7169·044 $\mu\mu$, and these are compared with the measurements of Bachem. An accuracy exceeding 0·005 $\mu\mu$ is claimed for the stronger lines. The measurements were made with the second order spectrum for wave-lengths below 5658 $\mu\mu$ and with the first order spectrum for larger wave-lengths. J. F. S.

Absorption Spectra of some Derivatives of *cyclo*Propane. EMMA P. CARR and C. PAULINE BURT (*J. Amer. Chem. Soc.*, 1918, **40**, 1590—1600).—In order to investigate further the effect of ring-formation on absorption spectra, the authors have examined a number of *cyclo*propane derivatives, their ethylenic isomerides, and the corresponding open-chain compounds. The series includes (1) methyl γ-benzoyl-β-phenylethylmalonate, methyl 3-benzoyl-2-phenyl*cyclo*propanedicarboxylate, and the two isomeric methyl β-benzoyl-γ-phenylvinylmalonates; (2) methyl anisoylphenylethylmalonate, methyl 3-anisoyl-2-phenyl*cyclo*propanedicarboxylate, and the two isomeric methyl β-anisoyl-γ-phenylvinylmalonates; (3) methyl benzoylphenylpropylmalonate and the isomeric methyl benzoyl-2-phenyl-3-methyl*cyclo*propanedicarboxylates; (4) αγ-dibenzoyl-β-phenylpropane, 1:3-dibenzoyl-2-phenyl*cyclo*propane, and 1:3-dibenzoyl-2-phenyl*cyclo*propene. (For preparation of these compounds, see Kohler and Conant, A., 1917, i, 566, 568.)

The authors find that the character of the absorption is closely related to the form of linking of the three central carbon atoms, and distinct differences in the absorption spectra of the corresponding cyclic, open-chain, saturated, and olefinic compounds are shown. In each series the cyclic substance shows an absorption quite similar to that of its open-chain analogue, but in every case the general absorption is greater. Evidently closure of the ring increases the absorptive power of the molecule.

Ring-formation in the *cyclo*propanes causes a shifting of the absorption towards the visible end, but to a less extent than in the case of the isomeric ethylenic compounds. These facts justify the conclusion that the *cyclo*propane ring is a centre of residual affinity similar in character, but intermediate in quantity to that of the double linking, and as such can form a conjugated system with a carbonyl group in the proper position.

The absorption spectra of four pairs of geometrical isomerides have been determined; in each pair the isomeride of lower m. p.

gave slightly greater general absorption and the isomeride of higher m. p. the greater tendency toward selective absorption. H. W.

Influence of Substituents of Reactions. III. Influence of Substituents on the Colour of Benzene Picrate. Hartwig Franzen (*J. pr. Chem.*, 1918, [ii], **98**, 67—80).—The problem has been previously investigated in a series of experiments on the rate of reduction of substituted phenylhydrazines (A., 1918, i, 456); as data can only be slowly accumulated in this manner, the author has sought a more convenient method, and has examined the absorption spectra of a series of picrates of benzene and its derivatives. He is led to the following conclusions: A relationship exists between the influence of a substituent of the first order on the rate of reduction of phenylhydrazine and on the colour of benzene picrate; a substituent which increases the rate of reduction of the hydrazine deepens the colour of the picrate. The activity of the substituent depends on the degree of unsaturation of the atom united to the ring carbon atom; depth of colour increases with the degree of unsaturation. If the latter is decreased by introduction of another atom, the colour becomes brighter. Among the picrates of benzene derivatives with substituents of the first order, the meta-compounds are always the least and the para-compounds the most intensely coloured; ortho-compounds occupy an intermediate position, and are only slightly darker than the meta-compounds.

H. W.

Phenomena of Luminescence in Pyrazoline Derivatives. Fritz Straus [with Carl Muffat and W. Heitz] (*Ber.*, 1918, **51**, 1457—1477).—See this vol., i, 41.

Chemiluminescence. I. Lifschitz (*Helv. Chim. Acta*, 1918, **1**, 472—474).—A preliminary account of work which is not yet completed.

Organomagnesium compounds of the type RMgX are very suitable for the study of chemiluminescence. Moeller (*Arch. Pharmaci Chemi*, 1914) has shown that the phenomenon only occurs with aromatic substances. It is now found that the difference between the aromatic and aliphatic compounds depends on the relative stability of the etherates; all ether-free Grignard reagents emit light in the presence of oxygen or nitrous oxide, but not of nitric oxide, nitrogen peroxide, carbon dioxide, and water. The additive compounds of organomagnesium substances with dimethylaniline are faintly luminescent in oxygen, but only in the case of aromatic derivatives.

The thermochemistry of the gradual addition of ether to suspensions of Grignard's reagents in benzene has been studied. With aliphatic reagents the greatest development of heat occurs when the first two molecules of ether are added, and very little heat is developed after the addition of four molecules; with aromatic reagents, on the other hand, the greater part of the heat is not

developed until four molecules of ether have been added, and further addition produces a still considerable effect. H. W.

Light Scattered by Gases; its Polarisation and Intensity. The Hon. R. J. Strutt (*Proc. Roy. Soc.*, 1918, [*A*], **95**, 155—176).—The light scattered at right angles by gases and vapours is not completely polarised. The vibrations parallel to the existing beam have always an appreciable intensity, which in ordinary cases varies from 1·2% (pentane) to 14% (nitrous oxide) of the intensity in the perpendicular direction. Helium is an outstanding case, polarising far less completely than any other gas. The measurements give an intensity in the parallel component nearly half as great as that in the perpendicular component. Theory indicates that this is the ratio to be expected if vibration in the helium atom is limited to a direction fixed within the atom, on the assumption of random orientation to the exciting light. Such an atom is the antithesis of the spherical atom or molecule which would give perfect polarisation. The intensity of scattering by the different gases tried varies as the square of the refractivity, within the limits of experimental error. Saturated vapours, even when very dense, show no increase of scattering power beyond what is expected from the density. If molecular aggregates are formed they are not numerous enough to show by this method. Liquid ether apparently scatters about seven times less light than a corresponding mass of ether vapour.

J. F. S.

Rotation Dispersion and Inversion of l-Menthone. Hermann Grossmann and Kurt Brauer (*J. pr. Chem.*, 1918, [ii], **98**, 9—66).—The rotation dispersion of *l*-menthone has been determined for a large number of solvents at 20°; the specific rotation (for $c=5$) varied from $-13°$ to $-25°$, and from $-35°$ to $-60°$ in red and violet light respectively. The dispersion-coefficient, $[\alpha]_r/[\alpha]_v$, lay between 2·16 and 2·80. Certain *d*-menthones have been obtained by inversion of *l*-menthone by concentrated sulphuric acid, according to Beckmann's method; determination of their dispersion-coefficients proves that they are not optical antipodes of *l*-menthone.

The rotation dispersion of *l*-menthone after being boiled with organic acids has been investigated in the actual solutions, which were found to be dextrorotatory, and the observations have been confirmed by examining the rotation dispersions of the menthones separated from such solutions either by water or by distillation. The values of $[\alpha]_r/[\alpha]_D$ lay between 3·12 and 3·67 for the solution and between 3·25 and 3·68 for the separated menthone. *l*-Menthone remains lævorotatory after being boiled with acetic anhydride; the dispersion-coefficient of the dissolved and separated menthone is abnormally low (1·73 and 2·01 respectively).

l-Menthone exhibits mutarotation when dissolved in formic acid or bromoform; the inversion in concentrated sulphuric acid solution

has been polarimetrically examined, and mutarotation has been observed.

The rotation-dispersion of *l*-menthone in alcoholic potassium hydroxide and hydrochloric acid solution has been investigated; the rotation is immediately positive, and is unchanged by heating. The value $[\alpha]_r/[\alpha]_r$ is unusually high, amounting to 4·35 or 3·87 for solutions and 5·07 or 5·57 for the separated menthones. When *d*-menthone is dissolved in alcoholic potassium hydroxide, the rotation falls noticeably, thus differing from its behaviour in formic and sulphuric acids, in which the rotation remains constant.

The gradual inversion of *l*-menthone at its boiling point has been investigated by a study of the rotation dispersion. An instance of abnormal rotation dispersion is here encountered, and the occurrence of a definite end-point, which is not altered by protracted heating, is established. The same end-point is reached more rapidly if *d*-menthone is used as initial material. The dispersion-coefficients at first decrease, then increase, and become infinitely great at zero, and subsequently sink until the value 3·47 is obtained; this value is exhibited by the so-called *d*-menthone.

The optical behaviour of *d*-menthones has been examined in a number of solvents; the specific rotation is found to be invariably increased in solution, whilst that of *l*-menthone is depressed. The dispersion-coefficients varied from 3·13 to 3·26.

The intra-molecular transformation suffered by *l*-menthone when heated appears to depend on desmotropy, equilibrium between the ketonic and enolic forms being slowly attained.

Inversion of *l*-menthone by various solvents is attributed to the additive or substitutive action of the latter, and the formation of *d*-menthone is due to a type of Walden inversion, this substance being formed by decomposition of intermediate products which are probably only stable in solution.

The influence of solvents on the specific rotation of optically active substances is due to reactions occurring between solvent and solute, for which the alteration in rotation is a particularly sensitive indicator. H. W.

Law of Blackening of Layers Sensitive to Light. F. Halla and A. Schuller (*Zeitsch. physikal. Chem.*, 1918, **93**, 173—182).—In a previous paper (*Zeitsch. wiss. Photochem.*, 1912, **11**) a relationship was put forward between the depth to which a film sensitive to light is darkened by light and the time of exposure. The relationships are now exactly and mathematically formulated. The calculations are extended to the case where the film lies on a reflecting base. The scattering of light is insufficient to explain the peculiarities observed in the blackening curves. The reflection of the base is shown to change, not only the depth of the blackening, but also the definition of the picture. J. F. S.

The Radioactive Properties of the Mineral Springs of Colorado. O. C. Lester (*Amer. J. Sci.*, 1918, [iv], **46**, 621—637).—The emanation content of more than 100 spring waters from Colorado

has been measured, and also the radioactivity of numerous samples of spring deposits. A high average activity of the waters was found, the most active examined showing the highest activity of any in the United States and surpassed only by a few foreign springs. For five springs the emanation content exceeded 100 (curies $\times 10^{-10}$ per litre), the highest being 305, and ninety-five springs exceeded 10. Of the latter, 75% were in or near metamorphic and igneous formations, but some of the most active were in sedimentaries. Thorium emanation was detected in only one spring. No springs of extraordinarily high emanation content were found, and although radioactive ores are abundant there are no large springs found near them. The measurements were for the most part carried out in the field by boiling out the water by Boltwood's method. F. S.

Thorium-Lead. KASIMIR FAJANS, F. RICHTER, and (FRL.) J. RAUCHENBERGER (*Sitzungsber. Heidelberger Akad. Wiss.*, 1918, pp. 28; from *Chem. Zentr.*, 1918, ii, 438—439).—According to theory, in addition to ordinary lead, there must be at least two members of the lead series with different atomic weights; on the one hand, radium-*G* or radium-lead, the final product of the uranium–radium series with an atomic weight 205·94, and, on the other, thorium-lead (Th-*D*), the atomic weight of which is calculated from that of thorium to be 208·08. Radium-*G* would be expected to occur in uranium minerals free from thorium, whilst thorium-lead must be looked for in thorium minerals free from uranium. The problem of isolating the latter is rendered difficult by the fact that thorium minerals free from uranium do not exist, whilst those poor in uranium are scarce. A mineral is unsuitable for investigation if it does not contain at least 4—5 times as much thorium as uranium, provided that thorium-lead and uranium-lead are either completely stable elements or have an approximately equal life period. The lead content of certain thorium minerals appears to point to the conclusion, however, that thorium-lead is relatively unstable, thus adding to the difficulty of its isolation.

The authors have examined a sample of thorite containing 30·10% of thorium, 0·44—0·45% of uranium, 0·35% of lead, in addition to unestimated amounts of silica, iron, rare earths, and traces of bismuth. The mineral was treated with fuming hydrochloric acid in glass flasks, in which decomposition is effected far more rapidly than in porcelain dishes. The solution was evaporated to dryness and the silica removed. Before precipitation of lead with hydrogen sulphide, the ferric iron was reduced to the ferrous state by means of hydroxylamine, and subsequent operations were conducted in an inert atmosphere. The lead was precipitated as sulphide, and converted first into the chloride and then into the sulphate, of which 4 grams were obtained. The mean of three analyses (performed by Hönigschmid) gave as atomic weight 207·90±0·013. On the supposition that uranium-lead and thorium-lead are perfectly stable elements, the whole of the lead separated from the thorite taken should have an atomic weight lying between the limits 207·97 and

208·00 if the atomic weight of thorium is taken as 232·12, that of helium as 4·00, and that of thorium-lead as 208·08. When the slight experimental and theoretical uncertainties are taken into consideration, the agreement between the practical (207·90) and theoretical (208·00) values may be regarded as satisfactory, and there is therefore no good reason for supposing that thorium-lead is not a stable element. If the slight discrepancy is actual, it is probably to be explained by the presence of ordinary lead (atomic weight 207·2); if, however, it is to be ascribed to the instability of thorium-lead, the lower limit for the half period of the element regarded as a uniform material is calculated to be $1·7 \times 10^8$ years. In any case, the existence of thorium-lead, obtainable in weighable amount and with an atomic weight approximating to 208·0, is placed beyond doubt. H. W.

Electrochemical Behaviour of Metals. A. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 158—171).—A theoretical paper, in which the relationships and equilibria between metal atoms, ions, and electrons are considered in the case of attackable metals (zinc) and non-attackable metals (nickel). These relationships are considered with regard to the potential difference between the metals and solutions of their ions and to the action of acids on the metals. In the first place, the consideration deals with equilibrium and velocity of the changes, both being considered in connexion with the Nernst solution theory, and in the second place the relationships are dealt with on the basis of the phase rule, Δx diagrams being evolved for the case of zinc and nickel as representing attackable and non-attackable electrodes. J. F. S.

Passivity of Chromium. III. A. H. W. Aten (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 138—150. Compare A., 1918, ii, 183, 193).—A theoretical paper, in which the reasons for the activation of passive chromium by cathodic polarisation are discussed. J. F. S.

Activation of Carbon Monoxide by Metallic Copper, the Generator Gas-cell and the Electromotive Activation of Alkali Formates. K. A. Hofmann (*Ber.*, 1918, **51**, 1526—1537). —The author's discovery (this vol., ii, 23) that carbon monoxide in the presence of oxygen is rapidly oxidised to carbon dioxide at the ordinary temperature at a copper surface moistened with an alkali hydroxide has enabled him to realise the generator gas-cell, O_2 | Cu | alkali | Cu | CO, and the drawbacks common to most of such cells have been overcome (subject of a censored patent). The *E.M.F.* ($CO \longrightarrow CO_2$) is found to be 1·32 volts at 20°, which compares well with the value 1·343 volts at 17°, calculated by Nernst and von Wartenberg from the dissociation of carbon dioxide. The present paper deals with the purely scientific aspect of the problem. It is shown that the activation of the carbon monoxide is not due to the formation of an alkali formate. The suggestion is made that

a labile *iso*formate, OH·C·OK, is produced; its formation is only minimal at the ordinary temperature when carbon monoxide and an alkali alone are present, but is stimulated in the presence of copper. C. S.

Dissociation of Strong Electrolytes. Niels Bjerrum (*Zeitsch. Elektrochem.*, 1918, **24**, 321—328).—A theoretical paper, wherein an hypothesis is developed according to which the strong electrolytes are completely dissociated. Because of the electrical forces between the ions, these electrolytes exhibit decreasing osmotic pressure, conductivity, and activity with increasing ion concentration. These decreases can be expressed by means of three numerical coefficients. A thermodynamic relationship between the activity and osmotic coefficients is developed and an approximate formula for the activity coefficient is worked out. The activity-coefficient possesses considerable chemical interest, and methods are outlined by means of which it may be determined, and in this connexion it is shown that the so-called neutral salt action, the anomalies of strong electrolytes, and the catalytic action of undissociated molecules only occur because the conductivity-coefficient has been used in calculations where more accurately the activity-coefficient should have been employed. J. F. S.

Ionic Migration in Liquid Crystals of Hydrated Ammonium Oleate. O. Lehmann (*Ann. Physik.*, 1918, [iv], **57**, 244—256).—The changes effected in the appearance of liquid crystals of hydrated ammonium oleate under potential differences of 0—100 volts have been studied microscopically and with the aid of crossed nicols. The liquid crystal was contained in a capillary of 0·06 cm. diameter, and contact made with two platinum electrodes by means of a drop of ammonia solution saturated with ammonium chloride. The appearance at the electrodes, using various potentials, is described, and it is shown that the main cause of the observed phenomena is the re-formation of the hydrate of ammonium oleate from the ions which have migrated from the tube, and the taking up of these by the molecules present. J. F. S.

Mechanism of Cathodic Metal Separation. V. Kohlschütter and E. Vuilleumier (*Zeitsch. Elektrochem.*, 1918, **24**, 300—321).—The electrolytic deposition of nickel from various solutions and under a series of different conditions has been studied with the object of finding an experimental connexion between the chemical polarisation and the form of electrolytically deposited metals. To ascertain this, the characteristic internal tension, which electrolytic nickel possesses, was investigated by depositing the metal on a platinum sheet and following the bending of the sheet. By this means it is shown that from the first moment the deposit undergoes a contraction which increases with further deposition. Consequently two processes must occur successively: first the formation of a film on the cathode, followed by a contraction of the film.

When the nickel is dissolved from such a contracted cathode the metal of the cathode returns to its original form. Consequently, the amount of bending corresponds with an equilibrium position, and the observation of the bending with time under stated conditions leads to characteristic curves. The process is dependent on the current density, and the composition of the electrolyte. It is strongly influenced by the addition of other substances to the electrolyte, and is less in solutions which cause an evolution of hydrogen, and also when the deposit is fine grained. When an already bent cathode is charged with hydrogen it straightens out again, but if the current is interrupted at this stage, the hydrogen is set free and the cathode takes up its original bent form. In solutions which do not evolve hydrogen the contraction occurs in jumps, which have the characteristics of delayed effects. The whole effect probably is due to the fact that the metal is at first deposited in a highly disperse form, and then the particles sinter with the formation of a denser material. This probably occurs along with the formation of a gas layer on the cathode, which plays the part of a dispersion medium. Since the electrolytic solution pressure of the highly disperse form is necessarily greater than that of the denser metal, this view explains the increase in the deposition potential above that of the ordinary metal. J. F. S.

The "Curie Point" of Pure Iron and Ferrosilicon. A. SANFOURCHE (*Compt. rend.*, 1918, **167**, 683—865).—It was shown by Curie that at about 1280° the magnetic property of iron was suddenly increased, in the ratio of about 3 to 2, and he termed this state of iron between 1280° and its melting point, δ. Pure iron prepared by the author melted at 1515°, and when slowly cooled its magnetic property suddenly changed at 1310°, whilst, on re-heating the iron, the break in the curve occurred at 1365°. This critical point is the "Curie point," A_4. The temperature at which it is shown is rapidly, though slightly, lowered by the addition of silicon in amounts up to 1% (1281°); above that amount the magnetic change is smaller, and with amounts of silicon in excess of 2·5% (1195°) is no longer perceptible. C. A. M.

A Relation between Boiling Points at One Atmosphere and in a "Vacuum." W. P. JORISSEN (*Zeitsch. anorg. Chem.*, 1918, **104**, 157—162).—Since the critical temperature of any substance is approximately equal to twice the boiling temperature (absolute) in a vacuum (20 mm.) and to 1·55 times the boiling temperature at atmospheric pressure, it follows that the ratio of the two boiling temperatures, $T_{(20\ mm.)}/T_{(1\ atm.)}$ is a constant, equal to 0·78. This ratio is shown to be constant for a large number of substances, both organic and inorganic. The constancy of the ratio can be deduced from van der Waals's vapour pressure formula and from the results of a number of independent workers. E. H. R.

Latent Heat of Fusion as the Energy of Molecular Rotation. Kôtarô Honda (*Sci. Rep. Tohuku. Imp. Univ.*, 1918, **7**, 123—130).—A theoretical paper, in which the author develops the equation $w\lambda/T_m = nE_{Tm}/2T_m$, in which T_m is the melting point in absolute degrees, E is the molecular energy belonging to each degree of freedom of the molecules, and $n=2$ or 3. This equation is tested by evaluating both sides and comparing the results for a number of elements. The equation is based on the assumption that during melting very little energy is required for internal or external work, and the numerical results show that for elements of group I this assumption is fully justified. In the case of a second group of elements which includes bismuth, tin, iodine, gallium, bromine, and chlorine, the values of $w\lambda/T_m$ are much greater than those for $nE_{Tm}/2T_m$. In the case of compounds, agreement between the two sides of the equation can be obtained if n is taken as larger than 2, that is, if the molecules have more than two degrees of freedom for rotation. This implies that compounds have a molecular structure both in the liquid and solid states. J. F. S.

The Course of the Values of a and b for Hydrogen at Different Temperatures and Volumes. III. and IV. J. J. van Laar (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 1—15, 16—25. Compare A., 1918, ii, 185, 291).—Theoretical papers, III. continuing the discussion of the pressure–volume relations in relation to the variability of a and b, whilst in IV. the value of a below the limiting temperature is discussed. A series of mathematical addenda to the previous papers are added. J. F. S.

Relationships between Absolute Temperatures and the Corresponding Absolute Pressures of Moist Vapours. O. Venator (*Zeitsch. physikal. Chem.*, 1918, **93**, 242—244).—A short, critical discussion of the van der Waals's equation and its corollaries. It is shown that the value of α is a variable one, having minima at the absolute zero and at the critical temperature, and increasing to a maximum as the temperature is raised or lowered respectively. J. F. S.

Raoul Pictet's Equation of Condition for Moist Vapours. O. Venator (*Zeitsch. physikal. Chem.*, 1918, **93**, 245—246. See preceding abstract).—A criticism of Pictet's equation of condition for moist vapours. It is shown that this equation may be expressed in the form of the van der Waals's equation, and further that neither of these equations supplies the needs of the physico-chemical technology. J. F. S.

Relationship between Absolute Temperature and Absolute Pressure in Kilograms per Square Cm. for Moist Vapours. O. Venator (*Zeitsch. physikal. Chem.*, 1918, **93**, 247—249. See preceding abstracts).—The author deduces from the van der Waals's

equation the expression $a=(T_k/T-1)/(\log p_k-\log p)$, in which T_k is the absolute critical temperature, p_k the corresponding pressure in kg./sq. cm., T any temperature between T_k and the absolute zero, p the pressure corresponding with T. J. F. S.

Negative Adsorption. L. Berczeller (*Biochem. Zeitsch.*, 1918, **90**, 290—293).—Negative adsorption was observed in experiments with starch as adsorbent with both lactose and maltose. With coagulated albumin, negative adsorption was observed with dextrose, lactose, maltose, and sucrose. S. B. S.

Dissociation of Salicylic Acid. R. Orthner (*Zeitsch. physikal. Chem.*, 1918, **93**, 220—235).—Salicylic acid, when heated at 200° under pressures of from 10 cm. to 120 cm. of mercury is dissociated into phenol and carbon dioxide to the extent of 98—82%. The decrease in dissociation with pressure is shown to be in accord with the law of mass action. J. F. S.

Reversal of the Dissociation of Salicylic Acid. R. Orthner (*Zeitsch. physikal. Chem.*, 1918, **93**, 236—239. See preceding abstract).—The dissociation of salicylic acid at 200° has been measured at various pressures of phenol and carbon dioxide. It is shown that just as the dissociation of salicylic acid follows the law of mass action, so the reversal of the dissociation by these substances is strictly in keeping with the requirements of the mass action law. J. F. S.

[**Dissociation of Salicylic Acid.**] Emil Baur (*Zeitsch. physikal. Chem.*, 1918, **93**, 240—241. See preceding abstracts).—A theoretical explanation of some of the points arising out of the previous papers. J. F. S.

Thickness of the Capillary Layer of Carbonic Acid. G. Bakker (*Zeitsch. physikal. Chem.*, 1918, **93**, 154—172).—A theoretical paper, in which methods of calculating the thickness of the capillary layer are deduced. These methods are then applied to the case of carbon dioxide. Making use of formulæ previously published (A., 1916, ii, 553), the equation $\epsilon=-A/(v+\beta)+f(t)$ is deduced for calculating the energy of the homogeneous phases. In this equation A represents an arbitrary temperature function. The equation is arrived at by neglecting a small factor of a general equation, and a correction to compensate for this is applied to the resulting energy value. From the same original formula the value of ζ, the thickness of the capillary layer, is calculated from the equation $-4T^2[d(H/\zeta T)/dt]=(\rho_1-\rho_2)r_i+2\{\epsilon_3-(\epsilon_1+\epsilon_2)/2\}(\rho_1+\rho_2)^2$; this equation may be integrated and the integration constant evaluated, since $H/\zeta T=0$ at the critical temperature. A third method of calculating the thickness of the capillary layer is afforded by means of the equation $\zeta=H/(p_N-p_T$ where p_N is the vapour pressure and p_T the pressure in the long direction of the capillary layer.

As mean values for carbon dioxide, by all three methods, the following are obtained for ζ:

t	−30°.	−10°.	0°.	10°.	20°.	25°.	30°.
ζ	1·46	1·72	1·91	2·21	3·51	7·06	26·1 $\mu\mu$

The differences between the values calculated by the different methods do not constitute an objection to the present theory, but are due to the differences of the equation of condition used.

J. F. S.

The Diffusion of Electrolytes into Jellies. I. The Relationship between the Distance of Diffusion and the Concentration. Otto von Fürth and Franz Bubanović (*Biochem. Zeitsch.*, 1918, **90**, 265—287).—Chlorides were allowed to diffuse into gelatin jellies containing silver nitrate, and the rate of diffusion could thus be measured by the silver chloride precipitate. If d = the distance of diffusion and k = concentration, it was found that after a time t, $d = mt^{\frac{1}{2}}k^n$, where m and n are constants. The constants vary with the properties of the jellies. n has the same value for the same jelly when different electrolytes are used. It has been found to vary between 0·10 and 0·31. S. B. S.

Dialysers made from Colloidal Membranes. L. Berczeller (*Biochem. Zeitsch.*, 1918, **90**, 302—304).—Some remarks on the adsorption of iodine by collodion membranes, and the alteration of the permeability of the membranes according to whether they are treated with water when the organic solvent is still in them or they are nearly freed therefrom. S. B. S.

Colloid Chemistry and its Industrial Application. F. G. Donnan, W. C. McC. Lewis, E. F. Armstrong, and A. S. Shorter (*Rep. Brit. Assoc.*, 1917, 20—105).—The first report of the committee appointed to compile information regarding the advances made in capillary and colloid chemistry with special reference to industrial processes. The various branches of the subject have been dealt with by specialists, and the following are included in the report: (1) viscosity of colloids, 3 pp., Emil Hatschek; (2) colloid chemistry of tanning, 15 pp., H. R. Procter; (3) general review and bibliography of dyeing, 19 pp., P. E. King; (4) colloid chemistry in the fermentation industries, 3 pp., Adrian J. Brown; (5) caoutchouc, 5 pp., Henry P. Stevens; (6) colloid chemistry of starch, gums, hemicelluloses, albumin, casein, gluten, and gelatin, 32 pp., H. B. Stocks; (7) colloids in the setting and hardening of cements, 4 pp., C. H. Desch; (8) nitrocellulose explosives from the point of view of colloidal chemistry, 2 pp., E. R. Chrystall; (9) celluloid from the standpoint of colloidal chemistry, 2 pp., E. R. Chrystall. Very full bibliographies are included in each of the sections. J. F. S.

Influence of Filtration on Hydrosols. Tadeusz Malarski (*Kolloid Zeitsch.*, 1918, **23**, 113—122).—The effect of filtration on

hydrosols of ferric hydroxide and silver, both alone and in the presence of electrolytes, has been determined by measuring the rate of motion towards the electrodes in an electric field. The experiments show that filtration, through filter-paper, fat-free cotton, glass wool, and sand has a very marked effect on the rate of motion of positive hydrosols and also on negative hydrosols the charge of which has been reduced or changed by the addition of electrolytes. This phenomenon is explainable by the theory of contact electrification. By successive filtration of ferric hydroxide sol through filter-paper, the potential difference of the double layer is diminished, and consequently the velocity in an electric field is also diminished; repeated filtration will reduce the potential difference to zero and finally change the sign of the charge. Solutions of silver which have been treated with aluminium sulphate so that macroscopic particles are visible on filtration become stable for weeks. This is to be explained by the retention of the aluminium ion by the filter-paper. J. F. S.

Spontaneous Transformation to a Colloid State of Solutions of Odorous Substances by Exposure to Ultra-violet Light. H. Zwaardemaker and F. Hogewind (*Proc. K. Akad. Wetensch. Amsterdam*, 1918, **21**, 131—137).—A number of solutions of odorous substances in water, glycerol, or paraffin are found after keeping for several weeks to have passed into the colloidal condition. The action is much more rapid in daylight than in the dark, whilst in the presence of ultra-violet light the action is still more rapid; in the case of many substances the transformation only occurs in the presence of ultra-violet light. The colloid particles are shown to be negatively charged. Among the substances examined, the following in decreasing order show a marked Tyndall cone: (1) in water solution: eugenol, cresol, guaiacol, carvacrol, citral, cumidine, thymol, and hypnone; (2) in glycerol solution: eugenol, safrole, cresol, nitrobenzene, and apiole; (3) in paraffin solution: aniline, eugenol, and cumidine.

J. F. S.

Amphoteric Colloids. I. Chemical Influence of Hydrogen-ion Concentration. J. Loeb (*J. Gen. Physiol.*, 1918, **1**, 39—60; from *Physiol. Abstr.*, 1918, **3**, 406).—At its isoelectric point, gelatin is undissociated. In acid solution, it forms cations only; in alkaline solutions, anions only. On the acid side of the isoelectric point, amphoteric colloids can combine only with anions of neutral salts; on the alkaline side, only with cations. At the isoelectric point, an amphoteric colloid cannot combine with either the cation or the anion of a neutral salt.

H. W. B.

Inversion of Sucrose by Colloidal Silicic Acid. Albert Mary and Alexandre Mary (*Compt. rend.*, 1918, **167**, 644—646).—Colloidal silicic acid, prepared by the action of hydro-

chloric acid on sodium silicate solutions and subsequent dialysis, hydrolyses sucrose fairly rapidly. The activity of the dialysed solutions begins to diminish after a period depending on the concentration of the colloid; 8% solutions retain their full activity for five to six hours, and 1·5% solutions for several months. Feeble hydrolysing power is exhibited also by solutions which have not been dialysed, but rendered faintly alkaline with sodium hydrogen carbonate solution; for these solutions there is an optimal temperature below 100°, varying according to the conditions, such as concentration of electrolytes. Coagulation of such solutions, whether spontaneous or accelerated by heating, is associated with loss of hydrolytic activity. If non-dialysed solutions are rendered faintly alkaline with sodium silicate solution instead of sodium hydrogen carbonate, they show a higher inverting power, and heating neither produces coagulation nor destroys their activity.

The conclusion is drawn that hydrolytic activity is a function of the degree of dispersion of the colloid, and that rise in temperature increases the activity (as in the case of acid hydrolysis), but eventually produces changes in the degree of dispersion, culminating in coagulation, which set a limit to the increase. The optimal temperature observed in inversion by colloidal metals and by invertase is probably to be accounted for on similar lines.

J. H. L.

Equilibrium between Carbon Monoxide, Carbon Dioxide, Sulphur Dioxide, and Free Sulphur. J. B. Fergusson (*J. Amer. Chem. Soc.*, 1918, **40**, 1626—1644, 1900).—The reaction $CO+\frac{1}{2}SO_2 \rightleftharpoons CO_2+\frac{1}{4}S_2$ has been studied, and the equilibrium constants at 1000° and 1200° have been determined. The experiments were made by the "stream" and "semi-stream" methods both with and without contact substances. As contact substances, broken porcelain and platinised porcelain were used. It is shown that in all probability small quantities of carbonyl sulphide are also formed. The experimental data have been used to calculate the thermodynamic constants of the reaction and the free energy equations of this reaction, and also of the formation of sulphur dioxide from its elements.

J. F. S.

Influence of Substitution in the Components of Binary Solutions Equilibria. XII. Binary Solutions Equilibria between Acid Amides and Phenols and their Derivatives. Robert Kremann and Alois Auer (*Monatsh.*, 1918, **39**, 441—493).—Fusion and solidification curves have been prepared for the following binary mixtures: (1) acetamide with the three nitrophenols, (2) benzamide with the three nitrophenols, (3) acetamide and salicylic acid, (4) benzamide and the three hydroxybenzoic acids, (5) acetamide and the three dihydroxybenzenes, and (6) benzamide with the three dihydroxybenzenes. Acetamide and *o*-nitrophenol form no compounds, but a simple eutectic at 41·2° with ca. 5% of acetamide. Acetamide forms compounds with equi-

molecular quantities of both *m*- and *p*-nitrophenol, which melt at 51·5° and 96·1° respectively. Benzamide and *o*-nitrophenol form no compounds, but a simple eutectic, m. p. 41·8°, with 5% benzamide. Benzamide and *p*-nitrophenol form an equimolecular compound, m. p. 97·2°. Acetamide and salicylic acid form a compound in the proportion of two molecules of the former to one of the latter, m. p. 108°, and a further compound in equimolecular quantities, m. p. 116°. Benzamide and *p*-hydroxybenzoic acid form a compound in equimolecular proportions, and also one with three molecules of benzamide to one molecule of *p*-hydroxybenzoic acid. Acetamide and quinol form an equimolecular compound, m. p. 101°; resorcinol and acetamide form a compound with two molecules of the latter to one of the former compound, m. p. 37·5°. Benzamide and quinol form a compound of two molecules of the former to one of the latter, m. p. 103·8; an equimolecular compound, m. p. 88·1°, is formed between resorcinol and benzamide. J. F. S.

Formation and Decomposition of Phloroglucinolcarboxylic Acid. G. Piazza (*Zeitsch. physikal. Chem.*, 1918, **93**, 183—219).—The equilibrium constant of the decomposition of the potassium salt of phloroglucinolcarboxylic acid, according to the equation $C_6H_2(OH)_3{\cdot}CO_2K + H_2O \rightleftharpoons KHCO_3 + C_6H_3(OH)_3$, has been determined by titration with standard acid, using fluorescein as indicator, and taking as the end of the titration that point at which the fluorescence just disappeared. The velocity of formation and decomposition of potassium phloroglucinolcarboxylic acid has been determined at 50°. The course of the reaction was followed by the refraction of a beam of light, and was observed by means of a Löwe's interferometer. The velocity of decomposition was also followed by titration and by electrical conductivity measurements. Contrary to the usually observed behaviour, it is shown that the formation occurs much more slowly than the decomposition. J. F. S.

The Inflammation of Mixtures of Methane and Air in a Closed Vessel. Richard Vernon Wheeler (T., 1918, **113**, 840—859).

Hydrolysis of Ethyl Acetate by Alcoholic Sodium Hydroxide. Rud. Wegscheider and (Frl.) Lilly Ripper (*Monatsh.*, 1918, **39**, 325—373).—The hydrolysis of ethyl acetate by solutions of sodium hydroxide in alcohol has been studied at 25°. The hydrolysis occurs according to the equation $dx/dt = [\text{ester}][\text{NaOH}][0{\cdot}12911(1-\alpha) + 0{\cdot}05710\alpha]$, in which α is the degree of dissociation of the base calculated from the dissociation constant. The undissociated molecules of the base hydrolyse more rapidly than the ions. If all the products remain in solution, the reaction follows the equation for second-order reactions, but with a concentration of sodium hydroxide above 0·38, the reaction takes

place more rapidly than the equation demands. The addition of sodium acetate increases the velocity of the hydrolysis. This depends on the total sodium concentration of the solution. The falling off of the velocity, which, according to the theory, ought to take place on account of the precipitation of sodium acetate, is so small as to be unrecognisable in this case. With increasing water concentration, the velocity increases very rapidly. If the sodium hydroxide solution is prepared by adding sodium to the alcohol, and the water content is so small that the whole of the sodium is not converted into hydroxide, then the velocity is very small and the reaction does not occur according to the equation for reactions of the second order. This is probably because the hydrolysis is effected by the sodium hydroxide, and not by the sodium ethoxide. When sodium hydroxide is dissolved in concentrated methylated spirit, a considerable contraction occurs. Experiments on the water content to determine the equilibrium conditions between alcohol, sodium acetate, and its trihydrate at 25° led to no definite result, but point to the fact that a water content of 4—5% is necessary. J. F. S.

The Relative Activity of certain Alkyl Iodides with Sodium α-Naphthoxide in Methyl Alcohol. Henry Edward Cox (T., 1918, **113**, 821—824).

Preparation of Catalytically Active Substances. Frieda Müller (D.R.-P. 307380; from *Chem. Zentr.*, 1918, ii, 492—493). —Werner's salts [that is, the double salts of the heavy metals and complex salts described by Werner (*Neuere Auschauungen auf dem Gebiete der organischen Chemie*, 1913)] are heated with exclusion of air at a temperature not exceeding that at which the catalyst is intended to be used. Heating may occur in a current of nitrogen or in a vacuum; if the product is to be used as catalyst for reaction between gases, the heating may take place in an atmosphere of one or all of the gases. Previous to heating, the substance may be distributed over carriers, such as clay or asbestos. For reactions between liquids and gases, the heating may proceed in the liquid after the salt has been dissolved, suspended, or emulsified. In many cases, it is necessary to heat under pressure. A catalyst from potassium chromicyanide at 300° gave 15% of ammonia at 300° and 120 atmospheres. Ammonia undergoes quantitative combustion in the presence of the product from luteochromium ferricyanide at 300°. Ammonium ferrimolybdate when heated at 400° in an atmosphere of nitrogen and hydrogen yields a loose, black powder which yields 19% of ammonia at 160 atm. and 400°. Ammonium sodium cobalticyanide is converted by ignition at 700° in nitrogen into a very porous, black catalyst for the synthesis of ammonia. Carbonatopentamminocobalt nitrate is heated at 420° in a current of nitrogen and hydrogen for the preparation of a catalyst. Up to 8% of formaldehyde could be

obtained from methane and oxygen at 150° by use of a catalyst from croceocobalt nitrate (heated in nitrogen at 150°). The catalyst from nitratopurpureocobalt nitrate is useful in the synthesis of ammonia. Indole is formed by hydrogenation of methyl *o*-toluidine in the presence of the catalyst from hexaquochromi-acetate. Borneol is converted into camphor in the presence of a product from hexaquochromi-propionate. A catalyst from cobalt hydroxonitrite brings about the quantitative oxidation of sulphur dioxide to sulphur trioxide by an excess of oxygen. H. W.

Hydrogenation and Dehydrogenation of Carbon Compounds with the Aid of Catalysts. Badische Anilin- & Soda-Fabrik (D.R.-P. 307580, 307989; from *Chem. Zentr.*, 1918, ii, 573, 693).—The conversion of organic compounds or of oxides of carbon into hydrogenated substances can be effected at relatively very low temperatures if contact agents are used which, in addition to the catalysing metal (metals of the platinum–palladium group are excepted), contain oxides of the earth metals, including the rare earths or of glucinum or magnesium. Satisfactory activation can only be secured by the use of very intimate mixtures. These may be prepared by simultaneous precipitation of the suitable hydroxides, oxides, carbonates, etc., from a solution of mixed salts, by heating mixtures of molten salts, and also, though not always with equal certainty and effect, by mechanical processes, such as very fine grinding, kneading in the moist state, pressing, etc.; when necessary, the mass is subjected to subsequent ignition and reduction. The production of highly active contact agents is greatly facilitated if at any rate the catalysing metal is formed from salts containing carbon, such as carbonates, formates, etc. The activity of the contact agent is frequently increased by adding compounds of the alkali metals, for example, sodium hydroxide, either to the mixture itself or to the materials from which it is prepared, a small quantity being frequently sufficient. It is sometimes advisable to add other organic or inorganic materials as carriers or binding material, or for the purpose of increasing the porosity of the mass; in such cases, the introduction of substances which, like chlorine, sulphur, phosphorus, and arsenic, can act as poisons, is best avoided. If reduction to the metallic state is necessary, it should be effected at as low a temperature as possible by pure hydrogen or other suitable agent. The catalytic activity of nickel, cobalt, and iron is particularly increased. The preparation of catalysts for the conversion of carbon dioxide into methane, the hydrogenation of oils, and the reduction of nitrobenzene is described.

The second patent describes the use of other difficultly reducible oxides of high melting point, particularly those of titanium, uranium, manganese, vanadium, columbium, or tantalum, in place of the oxides previously cited. Examples are given of the hydrogenation of cotton-seed oil and the hardening of earth-nut oil at 100—120°. H. W.

Negative Catalysts in the Hydrogenation of Oils. Seiichi Ueno (*J. Chem. Ind., Tokyo*, 1918, **21**, 898—939).—The degree of the hydrogenation of oils may be indicated by the formula $r=x/a$, where r represents the "ratio number of hydrogenation," x the difference between the iodine values before and after hydrogenation, and a the original iodine value of the oil. A comparison between the values of r and r' (the ratio number of hydrogenation in the absence of the particular substance) will show whether or no any given substance acts as a negative catalyst. By this means, various typical substances have been classified in accordance with their action on the catalytic hydrogenation of oils in presence of a nickel catalyst. Certain metallic soaps, such as those of potassium, barium, zinc, cadmium, lead, uranium, and gold, are injurious, whilst others, including those of calcium, aluminium, cerium, nickel, thorium, and platinum have no effect. Nickel salts of simple monocarboxylic acids, nickel lactate, and nickel salts of dicarboxylic acids (oxalic and succinic acids) have also no influence on the results. Copper hydroxide acts as a negative catalyst, but nickel hydroxide does not. Ammonium molybdate, boric acid, hydrochloric acid, and potassium hydroxide are pronounced poisons. Fatty acids, such as acetic, stearic, and oleic acids, have no effect, but hydroxystearic acids act as poisons, as do also hydroxy-acids, such as malic, citric, and tartaric acids. Certain powdered metals, such as tin, zirconium, and aluminium, have no marked action, but others, such as iron, lead, and zinc, are slightly poisonous. Other negative catalysts include sulphur, selenium, and tellurium, red phosphorus, glycerol, lecithin, alkaloids such as morphine and strychnine, potassium cyanide, and amygdalin. [See also *J. Soc. Chem. Ind.*, 1919, 20A.] C. A. M.

Catalytic Scission of Carbon Dioxide from Keto-carboxylic Acids. G. Bredig and R. A. Joyner (*Zeitsch. Elektrochem.*, 1918, **24**, 285—298).—The rate of decomposition of camphorcarboxylic acid into carbon dioxide and camphor by the bases quinoline, 2-methylquinoline, α-picoline, *s*-collidine, piperidine, pyridine, dimethylaniline, tribenzylamine, benzyldiethylamine, benzylamine, allylamine, tri*iso*butylamine, di*iso*butylamine, *iso*amylamine, tripropylamine, and diethylamine has been determined in the solvents acetophenone, *o*-nitrotoluene, and *m*-xylene. The reactions were carried out at 80·2°, and the rate was determined by weighing the carbon dioxide evolved. A series of determinations made to ascertain the equilibrium between acid and the various bases in *m*-xylene solution is described. These were carried out at 20·1°. A series of molecular weight determinations of the piperidine salts of a number of acids in benzene and ethyl alcohol solutions is also described. It is shown that the rate of decomposition of camphorcarboxylic acid in xylene, acetophenone, and *o*-nitrotoluene is practically the same in all cases, but in alcohol and water the decomposition is much slower. There is no direct connexion between the affinity constants of the

bases in water and the velocity of decomposition in the above-named solvents. The action of bases on the optical rotation of camphorcarboxylic acid was investigated, and it is shown that in *m*-xylene solution the simple Oudemann law does not hold, but in some cases the extent to which the salt is split up into acid and base can be determined. In *m*-xylene solution, the bases form acid complexes with an excess of the acid, in which more than one molecule of acid is combined with one molecule of base. In the extreme case, three molecules of acid are combined with one molecule of base. The velocity of decomposition of the salts is shown in the case of a series of bases to be parallel with the number of molecules of acid which combine with one molecule of base. It is probable that every carboxylic acid forms acid complexes with bases, but picric acid does not do so. Association of the acids only occurs in those solvents in which acid complexes with bases are formed, and the catalytic decomposition of camphorcarboxylic acid only occurs in those solvents in which acid complex formation takes place between the acid and base. J. F. S.

The Hydrolysis of Soap Solutions, Measured by the Rate of Catalysis of Nitrosotriacetonamine. James William McBain and Thomas Robert Bolam (T., 1918, **113**, 825—832).

Mercury as a Contact Poison. G. Bredig (*Ber.*, 1918, **51**, 1477).—The poisoning of catalysts by mercury (compare Paal and Hartmann, A., 1918, ii, 303) has been previously noticed by Bredig and Berneck (A., 1900, ii, 213) and others. C. S.

Whole Number Atomic Weights and Related Questions. R. von Mises (*Physikal. Zeitsch.*, 1918, **19**, 490—500).—A mathematical paper in which the probability that the atomic weights are whole numbers is treated. J. F. S.

The Atom Model of Bohr. Arthur Szarvassi (*Physikal. Zeitsch.*, 1918, **19**, 504—508).—A mathematical paper in which an attempt is made to explain certain insufficiently defined points in the theory of the structure of the atom as put forward by Bohr. J. F. S.

Atomic Structure. P. Debye and P. Scherrer (*Physikal. Zeitsch.*, 1918, **19**, 474—483).—A theoretical paper in which the rôle of the electron rings in the structure of crystals is discussed. It is shown that the electron rings of the carbon atom do not act as bonds in the structure of the diamond. The number of electrons accompanying the atoms in compounds is discussed, and some calculations are carried out in this connexion. The dimensions of the electron rings of the atoms are considered, and a method is worked out for calculating this quantity. Thus for the diamond it is shown that the radius of the electron ring is $0{\cdot}43 \times 10^{-8}$ cm., a figure which is in keeping with the value calculated by Bohr for

a ring in which four electrons are travelling round a nucleus containing four charges. In this case, the value is $0{\cdot}17 \times 10^{-8}$ cm.

J. F. S.

Theory of Röntgen Spectra. Fritz Reiche and Adolf Smekal (*Ann. Physik.*, 1918, [iv], **57**, 124—144).—A theoretical paper in which the relative positions of the K and L electron rings are discussed. Assuming the hypothesis of Debye and Vegard, and neglecting the electric and magnetic disturbances between the K and L rings, the formula $\Delta = v_{La}/R - 5/36z^2 = B_{p_1p_2} \cdot z + C_{p_1p_2}$ is deduced. In this equation, v_{La} is the vibration number of the L_a line, R the Rydberg number, z the atomic number of the element, $B_{p_1p_2}$ and $C_{p_1p_2}$ are functions of p_1 and p_2, the number of electrons in the K and L rings respectively. The values of v_{La}/R and $5/36z^2$ are evaluated for the elements of atomic numbers 30—92, and it is shown that up to 58 the agreement is linear, and above this number the divergence is very small, so that it becomes necessary to take the disturbances into account in such calculations.

J. F. S.

Coupling of Electron Rings and Optical Activity of Asymmetric Molecules. A. Landé (*Physikal. Zeitsch.*, 1918, **19**, 500—504).—A mathematical paper in which the connexion between the optical activity of asymmetric molecules and the electron rings is treated.

J. F. S.

Systematic Valency Theory and the Explanation on this Theory of Complex Compounds. Ionogen and Labile Bonds, Gaseous Molecules, Polymerisation and Isomerisation. Emil Kohlweiler (*Zeitsch. physikal. Chem.*, 1918, **93**, 113—153).—A continuation of the work previously published (A., 1918, ii, 304).—It is shown in the present paper that the views put forward to explain the formation and stability of compounds of the first order are equally applicable to compounds of higher orders. Particularly it is shown that the mechanism of the formation of molecular and complex compounds is the same as that of simple compounds in respect of the method of linking. The origin of ionogen and non-ionogen bands, polymerisation and isomerisation, the constitution of explosives and unstable compounds, and that of the gaseous molecules, are explained on the basis of this theory. For details of these points the original paper should be consulted.

J. F. S.

Apparatus for Facilitating the Manipulation of Gases. Max Bodenstein (*Ber.*, 1918, **51**, 1640—1645).—(1) A vacuum tube opener similar to that described by Stock (A., 1918, ii, 353) has been used by the author for more than twenty years. (2) A stopcock is described the extremities of the stopper of which are surrounded by the gas under manipulation, so that the intrusion of air is impossible. (3) A mercury gasometer is described which

requires the use of very little mercury. (4) A fatless metallic stopcock and (5) a quartz Bourdon manometer are also described. The first three pieces of apparatus are figured. C. S.

Condenser. R. Howden (*Chem. News*, 1918, **117**, 368).—The apparatus consists of a test-tube 2·5 cm. in diameter and 20 cm. long, which is placed in a vessel through which cold water is circulated. The tube is closed by a cork through which pass the tube from the distillation flask, and a second tube which extends from the bottom of the test-tube, the upper end of this second tube being bent downwards into a receiver. The first portion of the distillate collects in the test-tube; as further quantities collect, the contents of the test-tube are forced over into the receiver. W. P. S.

Two Lecture Experiments. Fr. Fichter (*Helv. Chim. Acta*, 1918, **1**, 430—432).—(1) *Absorption of Gases by Water.*—In demonstrating the absorption of very soluble gases by water, it is usual to collect them over mercury and then to admit water; in order to obtain the gas free from air and to collect over mercury without allowing it to escape into the atmosphere, the author recommends the use of a eudiometer, the upper end of which is drawn out into a tube connected through a stopcock with a T-piece. The eudiometer is filled with mercury up to the stopcock. The gas is then passed through the open limb of the T-piece until a test sample dissolves completely in water; it is then passed into the eudiometer by cautiously opening the cock. The experiment is completed as usual. (2) *Preparation of Calcium Carbide without an Electric Furnace.*—A quantity of compressed carbon dioxide snow is placed on an iron dish and covered with finely divided calcium mixed with loose solid carbon dioxide; reaction is started by allowing burning calcium to fall on the mixture, and proceeds vigorously. The presence of calcium carbide and nitride is demonstrated in the usual manner. Formation of the latter is inhibited as far as possible by using a considerable excess of carbon dioxide. The calcium must be in a finely divided state; large pieces only react superficially, and the presence of free calcium in the product causes the acetylene evolved, on addition of water, to be so largely diluted with hydrogen that it does not give a smoky flame. H. W.

Inorganic Chemistry.

The Determination of the Molecular Complexity of Liquid Sulphur. Alex. Mitchell Kellas (T., 1918, **113**, 903—922).

Occurrence of Hydrogen Selenide in Rain and Snow. P. Karrer (*Helv. Chim. Acta*, 1918, **1**, 499).—Repetition of Gassmann's experiments (A., 1918, ii, 309) has led the author to the conclusion that selenium is not present in snow or rain. H. W.

Starting and Stability Phenomena of the Oxidation of Ammonia and Similar Reactions. F. G. Liljenroth (*Chem. and Met. Eng.*, 1918, **19**, 287—293).—Conversion curves have been plotted for the oxidation of ammonia at various temperatures, showing that whilst little oxidation takes place at 400°, it rises rapidly between 450° and 500° to nearly 100%, reaches a maximum at about 750°, and then decreases first slowly and afterwards rapidly. The temperature of the gauze or catalyst may also be plotted for various percentages of ammonia-oxidation, and the curve is found to be a straight line, the position of the line, termed the "heat of reaction line," on the conversion curve diagram depending on (1) the initial temperature of the gas, and (2) the initial composition of the gas. The effects of changes in the velocity and the composition of the gaseous mixture on the relative positions of these two curves are described, and the conditions for (1) the cessation of the reaction, (2) overcoming the prejudicial effects of catalytic poisons, are indicated. The reaction does not start spontaneously, but must be initiated by heating to a particular ignition temperature, which is below the reaction temperature. The use of oxygen is shown to be not justified, as it merely results in a higher temperature, necessitating water cooling of the gauze. A cheap low-grade catalyst may be possible for the first gauze, and a platinum gauze for completion of the oxidation in a manner analogous to the sulphuric acid process. The synthetic ammonia process is also considered, and it is shown that in this case a heat exchanger must always be used, and additional heat must usually be supplied. With a high pressure and a good catalyst, however, no heat need be supplied except during the starting period.

B. N.

The Oxidation and Ignition of Coal. Richard Vernon Wheeler (T., 1918, **113**, 945—955).

Oxidation of Carbon Monoxide in Contact with Copper. K. A. Hofmann (*Ber.*, 1918, **51**, 1334—1346).—Continuing his search for a reagent to oxidise carbon monoxide at the ordinary temperature (A., 1916, ii, 637), the author has shown that hydrated

copper oxide in the presence of aqueous alkali converts carbon monoxide into a carbonate, although at only a slow rate. The addition of platinum metals, especially iridium, increases the rate five times. In contact with metallic copper moistened with aqueous alkali carbon monoxide mixed with air is oxidised two or three times more rapidly than it is when in contact with a copper oxide surface of the same area. The copper is converted into a peroxide, Cu_2O_3 or CuO_2, which is the real oxidising agent. The addition of a trace of iridium to the copper does not change the oxidising power of the peroxide, but increases the adsorptive capacity of the surface for carbon monoxide, and thus increases the rate of oxidation. It is very remarkable that the rate of oxidation of hydrogen in contact with an alkaline copper surface is only 1/70 (with addition of iridium, 1/50) of that of carbon monoxide, the copper surface having a very small capacity of adsorbing molecular hydrogen. The experiments were performed in a Hempel gas pipette filled with rolls of copper gauze moistened with 15% potassium hydroxide solution. The concentration of the alkali does not appreciably affect the results. C. S.

The Action of Chlorine on the Alkali Iodides. William Norman Rae (T., 1918, **113**, 880—884).

Literature on the Solubility of Systems Relating to Nitre Cake. H. W. Foote (*J. Ind. Eng. Chem.*, 1918, **10**, 896—897).—A résumé of the literature dealing with the solubility relationships of the systems, Na_2SO_4–H_2SO_4–H_2O; Na_2SO_4–RSO_4–H_2O; and RSO_4–H_2SO_4–H_2O (R = Fe″, Cu, Ba, Ca, Gl, etc.). J. F. S.

Recrystallisation of Nitre Cake. Blair Saxton (*J. Ind. Eng. Chem.*, 1918, **10**, 897—901).—Equations, based on solubility determinations, have been developed, by means of which the amount of any one solid phase, that can be separated from the system Na_2SO_4–H_2SO_4–H_2O, can be calculated if the composition of the original nitre cake and the acid concentration after crystallisation are known. These equations are for the temperature 25°. Further equations are given for the same temperature, by means of which the amount of water to be added to the nitre cake may be calculated in order to leave a calculated amount of one of the solid phases. Further equations for obtaining the maximum amount of each solid phase from solution at temperatures of 0° and 25° are also given. Leaching processes are outlined, by means of which sulphuric acid may be concentrated in the solution and sodium sulphate in the solid. It is found experimentally that this separation can be carried out more efficiently at 0° than at 25°. J. F. S.

Colloidal Silver. Alwyn Pickles (*Chem. News*, 1918, **117**, 358).—When well-washed silver oxide is reduced by a rapidly stirred 60% solution of formaldehyde, a solution of colloidal silver is produced. This solution is very stable, and varies in colour from pale

lilac to rich ruby-red. Acetaldehyde has not the same effect, and with formaldehyde the coloured solutions are only produced at about 35°. The colour is discharged slowly by salt solutions, and by nitric acid. Hydrogen peroxide is slowly decomposed by the solution. J. F. S.

Rational Preparation of Superphosphates. A. Aita (*Annali Chim. Appl.*, 1918, **10**, 45—103).—On dissolving increasing quantities of monocalcium phosphate in a given weight of water at constant temperature the proportion of free phosphoric acid continually increases, and tends towards a limit in accordance with the equation

$$2CaH_4(PO_4)_2 \rightleftharpoons CaH_4(PO_4)_2 + CaHPO_4 + H_3PO_4.$$

Up to the saturation point at 15° there would thus be a liquid phase consisting of water, monocalcium phosphate, and free phosphoric acid, and a solid phase consisting solely of dicalcium phosphate formed by hydrolysis of the monocalcium phosphate. Beyond the saturation point, with increasing quantities of calcium oxide and phosphoric oxide, the liquid phase remains unaltered, whilst the solid phase is constantly enriched by monocalcium phosphate. On raising the temperature the decomposition of the monocalcium phosphate is accentuated, whilst the saturation point is retarded. Monocalcium phosphate appears in the solid phase at the same limit of concentration for the calcium oxide, but at a greater concentration of the phosphoric oxide. In the case of commercial superphosphates containing about 12—20% of soluble phosphoric oxide and 10—20% of water, there is a system with a fairly high proportion of phosphoric oxide, and a very low proportion of water. In estimating free phosphoric acid in such products it is necessary to use anhydrous ether for the extraction, since water, alcohol, or ordinary ether cause more or less hydrolysis of the monocalcium phosphate, according to the amount of water originally present. The physico-mechanical properties of superphosphates depend on the proportion of free phosphoric acid and water, the former depending on the nature and physical conditions of the components of the reaction, and the latter mainly on the concentration of the sulphuric acid used in the preparation. On these grounds commercial superphosphates may be classified as *normal* or *abnormal* products, the former containing not more than 10—12% of water or 1—2% of phosphoric oxide as free phosphoric acid (about 5—10% of the total soluble phosphoric oxide). Dicalcium phosphate is invariably present, and the fraction of phosphoric oxide in that form of combination should be equal to that present as free phosphoric acid. The mono- and di-calcium phosphates and calcium sulphate are mainly present in the hydrated form. In the case of superphosphates of abnormal constitution the water of the liquid phase exceeds 12%, and the free phosphoric acid exceeds 2% or 10% of the soluble phosphoric oxide, whilst the salts are mainly in the crystalline condition, and there is little or no dicalcium phosphate present. It is commonly

accepted, in accordance with Kolb's view, that the reaction between sulphuric acid and mineral phosphates takes place in two stages:

$$3Ca_3(PO_4)_2 + 6H_2SO_4 = 4H_3PO_4 + Ca_3(PO_4)_2 + 6CaSO_4,$$
$$Ca_3(PO_4)_2 + 4H_3PO_4 = 3CaH_4(PO_4)_2,$$

but the observed facts show that the main reaction is more correctly represented by the equation:

$$5Ca_3(PO_4)_2 + 11H_2SO_4 = 4CaH_4(PO_4)_2 + 2H_3PO_4 + 11CaSO_4.$$

The influence of raising the temperature on the reaction is to increase the concentration of free phosphoric acid in the liquid phase, whilst in the solid phase the dicalcium phosphate increases in equal proportion with the free phosphoric acid. These constituents gradually interact to form monocalcium phosphate, so that the existence of dicalcium phosphate in an industrial product will depend on the proportion of free phosphoric acid originally present. Hence in products prepared with an excessive quantity of sulphuric acid, and thus containing a high proportion of free phosphoric acid, the dicalcium phosphate will be reduced or disappear altogether. In fact, monocalcium phosphate is not hydrolysed in presence of an excess of phosphoric acid, and in such cases the solid phase of the system will consist solely of monocalcium phosphate. The application of these principles to the industrial preparation of superphosphates yields products with the desired physico-mechanical properties. [See also *J. Soc. Chem. Ind.*, 1919, 23A.] C. A. M.

The Decomposition of Barium Peroxide and the Reactivity of the Resulting Barium Oxide. J. Arvid Hedvall (*Zeitsch. anorg. Chem.*, 1918, **104**, 163—168).—The decomposition of barium peroxide by heat at atmospheric pressure has been followed by means of the heating curve. The peroxide was heated in a carbon tube furnace and the temperature recorded at 10 sec. intervals by means of a platinum—platinum–rhodium thermo-element. The reaction being endothermic, its range is indicated on the heating curve by a pronounced flattening towards the time axis. The temperature at which the vapour pressure of the evolved oxygen is equal to 760 mm. was found to be 795°. This agrees with the value 796° found by Le Chatelier. The higher temperature, 825°, obtained by Hildebrand is accounted for by the fact that this observer used very carefully dried materials, for in the absence of moisture the reaction is very slow and incomplete.

In presence of copper oxide, barium peroxide starts to decompose at about 200°, the reaction becoming most vigorous at 625—660°, as shown by the heating curve. When the peroxide is heated with amorphous silica, however, the rate of rise of temperature increases above 400°. The endothermic decomposition of the peroxide is evidently accompanied by a more strongly exothermic reaction, probably the formation of a barium silicate, brought about by the great reactivity of the barium oxide at the moment of its formation. Even when powdered quartz glass or crushed quartz is used

in place of amorphous silica, there is evidence in the heating curve of silicate formation. E. H. R.

Solubility of Cupric Hydroxide, to a Certain Concentration in Sodium Hydroxide and Potassium Hydroxide. Ed. Justin-Mueller (*Compt. rend.*, 1918, **167**, 779—780).—Cupric hydroxide dissolves in aqueous sodium hydroxide (D 1·345—1·370) or aqueous potassium hydroxide (D 1·453—1·498) to the extent of 0·78 gram in 100 c.c., giving bright blue solutions which do not give any precipitate when boiled directly or first diluted and then boiled. Solutions prepared with more dilute alkali are not stable. W. G.

Scandium from a Brazilian Source. C. James (*J. Amer. Chem. Soc.*, 1918, **40**, 1674).—Whilst working up quantities of Brazilian zirconia the author obtained a gelatinous residue which on examination was shown to consist of scandium fluoride. J. F. S.

Rare Earths. VIII. Separation of Yttrium from Erbium; The Ratio $Er_2O_3 : 2ErCl_3$. Edward Wichers, B. S. Hopkins, and C. W. Balke (*J. Amer. Chem. Soc.*, 1918, **40**, 1615—1619. Compare A., 1917, ii, 34).—Using material containing only erbium and yttrium, the authors have investigated the newer methods proposed for the separation of these two elements. The cobalticyanide and the nitrite precipitation methods were found to give good results, the latter being the more efficient and practicable. The older nitrate fusion method was found to give results far superior to the other methods, and by this method erbium compounds of a high degree of purity were obtained. The ratio of erbium oxide to erbium chloride was determined in seven analyses. The ratio was found to vary with the temperature and length of time of ignition of the oxide. Erbium oxide, prepared by the ignition of the oxalate and ignited for several hours at 800° and two hours at 900°, was found to retain considerable amounts of carbon dioxide. This is contrary to Hofmann's results (A., 1910, ii, 1073), and consequently brings into disrepute the present accepted value of the atomic weight of erbium. Until erbium oxide of the definite composition Er_2O_3 is prepared, no ratio in which the oxide is one term can be trustworthy for the purpose of atomic weight determinations. J. F. S.

Preparation and Properties of Yttrium Mixed Metal. J. F. G. Hicks (*J. Amer. Chem. Soc.*, 1918, **40**, 1619—1626).—Experiments of a preliminary nature dealing with the preparation of yttrium mixed metal are described. It is shown that the method of preparing anhydrous chlorides of the metals of the yttrium earths, by heating the hydrated chlorides with ammonium chloride to drive off five of the six molecules of water of crystallisation, and then in a current of hydrogen chloride to remove the

last molecule of water, is capable of being used on the large scale. The mixed metal has been prepared in the form of powder by heating the anhydrous chlorides with sodium in a vacuum at 1100°, and also by electrolysing a mixture of the molten chlorides in a protected graphite crucible, using a graphite anode. Electrolysis of a solution of the mixed oxides in fused cryolite also yields the mixed metal in the form of powder, but the method is less efficient than the foregoing methods. In all these processes, there is considerable loss of yttrium chloride, owing to its volatility at the temperature of the experiments. The powdered products have been obtained in a coherent form by sintering in a vacuum, but the resulting mass easily disintegrates. The product obtained has a mean "atomic weight" of 120 and contains 94·05—95·70% of metal, which corresponds with 37·5% of yttrium. It burns in the air at a dull red heat with a very bright light, and yields a light brown oxide. It is slowly oxidised by moist air at the ordinary temperature. It glows when heated in hydrogen, nitrogen, or carbon dioxide. It does not amalgamate with mercury, and is readily attacked by water. Yttrium mixed metal is pyrophoric, but not so strongly as the cerium metal iron alloys. J. F. S.

Effects of Heat on Chemical Glassware. R. G. Sherwood (*J. Amer. Chem. Soc.*, 1918, **40**, 1645—1653).—When glass is heated, there is shown to be evidence of two distinct kinds of gaseous evolution, that resulting from adsorbed material, which is readily removed at temperatures below 300°, and that resulting, in all probability, from a decomposition of the glass itself. The latter effect becomes important above 400° for the softer glasses and above 500° for the harder glasses. There is some evidence of a definite characteristic rate of gaseous evolution for each temperature to which glass is subjected, increasing with the temperature and extending over a considerable period. Observations on one sample at 500° showed a small, continuous evolution even after heating for twenty hours. Adsorption products are confined to quantities which are represented approximately by a layer of gas about one molecule deep, and are removed with much greater rapidity at lower temperatures than the other products obtained, which are due to the heating of the glass. The most important of the gaseous evolution products obtained from glass under the influence of heat is water, which, as the temperature is raised to the softening point of the glass, constitutes almost the entire quantity of the evolution, but its amount at a lower temperature may be relatively unimportant. J. F. S.

Plasticity and 'Strength' of Clay. Otto Nolte (*Zied. Zentr.*, 1918, **47**, 108—109).—Extraction of a heavy Silesian clay with alcohol and ether did not cause any diminution in the plasticity or 'strength' of the clay. The presence of a certain proportion of organic matter, therefore, does not affect these qualities of the clay. The extract was found to contain sulphur and an organic compound which was not identified. H. W. B.

Zirconyl Basic Chromate. F. P. Venable and L. V. Giles (*J. Amer. Chem. Soc.*, 1918, **40**, 1653—1656).—A basic zirconium chromate is prepared as a granular, yellow precipitate by dissolving zirconium hydroxide in a boiling solution of chromic acid, diluting, and again boiling the solution. The compound obtained loses a considerable quantity of its water at 110°, but the whole of it is only lost at 200°. The compound is shown to have the formula $2ZrO(OH)_2,ZrOCrO_4,8H_2O$, and it is suggested that its formation occurs as follows: first, normal zirconium chromate is formed, which is immediately hydrolysed to $ZrOCrO_4$; some of the zirconium hydroxide is partly dehydrated to give $ZrO(OH)_2$. These two substances then combine to give the yellow, insoluble compound described above. The present work is at variance with earlier work on zirconium basic chromates by Haber (A., 1897, ii, 295). J. F. S.

Antimonic Acids and Antimonates. Gerhardt Jander (*Kolloid Zeitsch.*, 1918, **23**, 122—144).—Analyses of the various hydrates of antimony pentoxide have been made, and the dehydration curves of these compounds obtained by keeping them over sulphuric acid in a desiccator. The behaviour of the antimonic acids toward hydrochloric and sulphuric acids and toward solutions of potassium and sodium hydroxides has been studied. The potassium and sodium salts of these acids have also been investigated. The experiments show that the properties of the antimonic acids vary with the method of preparation and with previous treatment. Thus, modifications which differ in their water content, stability, solubility, and their behaviour towards acids and alkalis are obtained (i) by the action of water on the pentachloride, (ii) by the action of acids on antimonates, and (iii) by the hydrolysis of the trichloride in the presence of nitric acid. These varieties of antimonic acid differ only slightly from one another, and probably, as in the case of the stannic acids, the difference is due to a difference in the size of the particles. The experiments indicate that the tri- and tetra-antimonic acids, that is, the soluble antimonic acids, are hydrosols of small stability, and that the definite hydrates of antimony pentoxide known as ortho-, pyro-, and meta-antimonic acid can have no free existence. The hydrates of antimony pentoxide exhibit a marked selective absorption towards dilute alkalis. Thereby are formed amorphous substances, which apparently are alkali antimonates. The composition of these substances, however, varies continuously with the composition of the solid hydrate. In concentrated alkali solutions, the hydrates of antimony pentoxide dissolve, and from these solutions at low temperature and by careful evaporation, various alkali antimonates may be crystallised, but the nature of the salt depends on the concentration of the mother liquor. The compound

$$1{\cdot}71K_2O,Sb_2O_5,8H_2O$$

has been obtained in this way. J. F. S.

Bismuth Hydride. Fritz Paneth (*Zeitsch. Elektrochem.*, 1918, **24**, 298—299).—Working from the point of view that isotopes and their compounds are identical, the author is of the opinion that bismuth hydride is capable of existence, and that it is gaseous and only moderately stable, much less so than antimony hydride. These statements are based on the fact that by the action of hydrochloric acid on magnesium which has been covered with thorium-*C* (an isotope of bismuth), a radioactive hydride is produced which has the properties enumerated above. J. F. S.

Hydroxylamine Platinum Bases. Leo Alexandrowitsch Tschugaev and Ilja Iljitsch Tschernjaev (T., 1918, **113**, 884—897).

Mineralogical Chemistry.

"Hydromagnocalcite" from the Tatra Mountains, Carpathians. Emanuel Glatzel (*Centr. Min.*, 1918, 307—311).—The compact, chalk-white material with conchoidal fracture is found as loose blocks in the Lopusna valley, near the village of Lucsivna, on the southern slopes of the Tatra Mountains. Analysis gave results approximating to the formula $CaCO_3 + Mg(OH)_2$.

CaO.	MgO.	CO_2.	H_2O.	Total.	Sp. gr.
36·55	23·15	28·75	10·60	99·05	2·412

[This is evidently pencatite, which was long ago proved to be a mechanical mixture of calcite and brucite ($Mg[OH]_2$).] L. J. S.

Analytical Chemistry.

Quantitative Analysis of Small Quantities of Gases. H. M. Ryder (*J. Amer. Chem. Soc.*, 1918, **40**, 1656—1662).—A somewhat complicated apparatus is described by means of which a quantitative analysis of 5 cu. mm.—1 c.c. of a gaseous mixture of water vapour, carbon dioxide, carbon monoxide, oxygen, hydrogen, nitrogen, and methane may be carried out with an accuracy of about 5% for each constituent. The apparatus makes use of a McLeod gauge and an optical lever gauge, but for details the original should be consulted. J. F. S.

Gas Bubbler for Gas Analysis. Oliver D. Burke (*Chem. News*, 1918, **117**, 368—369).—The glass tube through which the

gas enters is drawn out into a fine capillary. Another glass tube is fused on to the side of the first tube and bent so that the end extends just below the end of the capillary, where it is flattened and the top surface ground. The capillary is made to fit tightly on the ground surface, so that the gas escaping from the capillary is broken up into very fine bubbles. [See, further, *J. Soc. Chem. Ind.*, January, 1919.] W. P. S.

Oxidising Action of Potassium Dichromate as Compared with that of Pure Iodine. Carl R. McCrosky (*J. Amer. Chem. Soc.*, 1918, **40**, 1662—1674).—The author has studied the trustworthiness of potassium dichromate as a standardising agent in iodometric determinations. It is shown that potassium dichromate always liberates more than the theoretical quantity of iodine from hydriodic acid. This excess of iodine may be reduced, but not wholly removed, by removing dissolved air from the solutions, by drying, and fusing the dichromate in the absence of air and by recrystallising repeatedly to remove oxidising impurities. It is also shown that the excess of iodine is not due in any way to the catalytic action of chromium chloride. J. F. S.

Estimation of Active Oxygen in Sodium Peroxide. Jaroslav Milbauer (*J. pr. Chem.*, 1918, [ii], **98**, 1—8).—The following methods have been proposed for the estimation of active oxygen in sodium peroxide: (1) liberation of hydrogen peroxide by water followed by titration with potassium permanganate, (2) treatment of sodium peroxide with potassium iodide and potassium hydrogen carbonate, and titration of the iodine liberated with sodium arsenite, and (3) measurement of the oxygen liberated by water in the presence of cobalt nitrate. The results obtained by the first method are very low, those by the second are somewhat better, but still low, whilst the third method gives high results. The methods have been critically examined and improved; the following processes yield accurate results: (1) Water (100 c.c.) is mixed with concentrated sulphuric acid (5 c.c.) and chemically pure boric acid (5 grams); sodium peroxide (0·5 gram) is gradually added to the mixture, which is kept briskly shaken, and the liberated hydrogen peroxide is titrated with potassium permanganate. The usual permanganate method gives low results, since a portion of the hydrogen peroxide is catalytically decomposed by the manganese sulphate formed during the process. (2) Sodium peroxide is gradually introduced into a solution of potassium iodide (2 grams) in dilute sulphuric acid (1 in 20; 200 c.c.); the iodine is titrated with standard thiosulphate. The results agree fully with those obtained by the permanganate method. (3) Sodium peroxide (0·2—0·3 gram) is mixed with about 10 c.c. of copper sulphate solution (0·05%) in a small flask connected to a nitrometer; the flask is shaken, and decomposition is complete within a minute, when the liberated oxygen is measured. The gas evolved contains about 0·32% of carbon dioxide and 0·08% of

hydrogen. With cobalt nitrate as catalyst, the results are invariably high; the authors consider this may indicate the presence of an oxide higher than the peroxide.

The action of the atmosphere on sodium peroxide has also been investigated; moisture appears to be more active than carbon dioxide in causing decomposition. H. W.

Pregl's Micro-estimation of Nitrogen. Hans Fischer (*Ber.*, 1918, **51**, 1322—1325).—The estimation of nitrogen in difficultly combustible substances by the micro-Dumas method (compare Dubsky, A., 1918, ii, 130) gives untrustworthy results, and the author now employs only the original Pregl method. The causes of the inaccuracies in the former method are discussed.

The author uses the micro-Pregl method in preference to the Lassaigne test for the detection of nitrogen in rare or very valuable organic compounds. C. S.

Detection and Estimation of Hydrogen Phosphide in Hydrogen. J. Soyer (*Ann. Chim. anal.*, 1918, **23**, 221—225).—Hydrogen prepared by the action of sodium hydroxide on ferrosilicon always contains traces of hydrogen phosphide. The presence of the latter may be detected by burning the hydrogen from a platinum jet and directing the flame on to the edge of a porcelain basin; the flame has a green coloration. When examined with the spectroscope, the flame exhibits the phosphorus spectrum. If a drop of water suspended on a glass rod is held in the flame for fifteen seconds and then tested with molybdic acid reagent, a yellow precipitate is obtained. The amount of hydrogen phosphide present is estimated by passing a definite volume (from 2 to 20 litres) of the gas, together with a large excess of air, through a platinum jet arranged in a silicon tube heated to bright redness; this tube is inclined slightly, and its lower end is connected with absorption vessels containing water. When the desired quantity of the gas has been burned, the tube and the contents of the absorption vessels are rinsed into a basin, treated with 5 grams of ammonium nitrate, concentrated to about 40 c.c., and the phosphoric acid precipitated with molybdic acid reagent. [See, further, *J. Soc. Chem. Ind.*, 1918, 765A.] W. P. S.

Estimation of Minute Quantities of Arsenic. O. Billeter (*Helv. Chim. Acta*, 1918, **1**, 475—498).—A more extended and somewhat modified account of the method previously published (A., 1915, ii, 578).

The estimation of arsenic in organic substances is effected in the following manner. The organic matter is destroyed either by treatment with a mixture of nitric and concentrated sulphuric acids or, in the case of urines, by rendering the latter alkaline with sodium carbonate, evaporation to a syrup, admixture with potassium perchlorate (2 grams) and potassium sulphate (4 grams) for each 100 c.c. of urine, desiccation of the mixture at 120°, and

gradual introduction of the latter into a platinum crucible heated to dull redness, followed by more intense ignition until tranquil fusion is attained. The arsenic is separated from other metals by distillation with a mixture of sodium chloride (2 grams) and potassium bromide (0·2 gram) for each 20 c.c. of sulphuric acid (the addition of hydrazine sulphate previously recommended is found to be unnecessary), or, if destruction of organic matter has been effected with potassium perchlorate, by treatment with potassium bromide (0·1—0·2 gram) and sulphuric acid (90%, 6 c.c.). Mercury is completely retained by one distillation, but if antimony is present, it is necessary to redistil after addition of 5—6 grams of sulphuric acid (90%). Hydrochloric acid is eliminated from the distillate by treatment with hypochlorous acid, and the solution is evaporated to dryness. The residue is dissolved in sulphuric acid (12%, 1 c.c.) and evaporated on the water-bath to destroy any chloric acid that may be present; after addition of water (0·85 c.c.), it is transferred to a Marsh's apparatus. By this method, 0·01 mg. of arsenic may be detected.

The precautions necessary for ensuring the requisite purity of the reagents are fully described. The commercial pure sulphuric acid is diluted to 85% and heated with sodium chloride (3%) and potassium bromide (0·3%) in a quartz flask; the treatment is twice repeated with smaller quantities of salts, and the acid is finally distilled from a quartz retort and collected in a quartz flask. The nitric acid and the salts are purified by Lockemann's method. Zinc is conveniently obtained by the electrolysis of an aqueous solution of zinc sulphate, using a zinc anode and copper cathode; the metal is obtained in the pulverulent state, and dissolves readily in dilute sulphuric acid without being activated. It is free from arsenic. Hypochlorous acid is best prepared by the solution of chlorine monoxide in water.

The sensitiveness and constancy of the arsenic mirrors depend considerably on the quality of the calcium chloride used in desiccating the gas. Commercial fused calcium chloride is unsuitable, as it is always strongly alkaline; a neutral product can be obtained by dehydrating the crystalline substance at 200°, and subsequently gradually heating the finely divided product to its melting point in a quartz tube in a slow current of dry hydrogen chloride. The best results are obtained by starting from metallic calcium.

H. W.

Amount of Amorphous Silica in the Soil. Béla von Horváth (*Bied. Zentr.*, 1918, **47**, 97—98).—For the estimation of the amorphous silica, 5 grams of the soil are extracted with 100 c.c. of a 1% sodium carbonate solution for fifteen minutes at 100°. Solutions of sodium carbonate of greater concentration than 1% dissolve silicates and quartz besides amorphous silica, the results obtained being consequently too high. When estimated by the author's method, soil is found to contain only a few milligrams per cent. of amorphous silica.

H. W. B.

Estimation of Metals by Electrolytic Deposition without using an External Supply of Electricity. MAURICE FRANÇOIS (*Compt. rend.*, 1918, **167**, 725—727).—A strip of nickel is placed across the top of a platinum crucible, and a zinc rod, 5 mm. in diameter, is suspended from the strip; the rod is notched so as to fit on to the nickel strip, and the lower end of the rod extends nearly to the bottom of the crucible. The zinc rod is amalgamated at least twenty-four hours before being used, and is wrapped in filter-paper, which is tied on to the rod with ordinary cotton thread. The electrolyte used for the deposition of silver or gold consists of 9 c.c. of 10% potassium cyanide solution, 5 c.c. of potassium hydroxide solution (D 1·332), and 2 c.c. of ammonia; for the deposition of mercury, the solution should consist of 20 c.c. of 10% sulphuric acid containing 0·5 gram of potassium iodide. In all cases, the deposition requires twenty-four hours for completion. [See, further, *J. Soc. Chem. Ind.*, 1918, 784A.]

W. P. S.

Quantitative Estimation of Ions by Microanalytical Methods. I. ROBERT STREBINGER (*Österr. Chem. Zeit.*, [ii], **21**, 71—73; from *Chem. Zentr.*, 1918, ii, 471).—The author has extended Pregl's method of quantitative organic microanalysis to inorganic substances, and describes the estimation of silver, nickel, arsenic, iron, chromium, and copper, and the separations of silver from copper and lead from tin. Precipitation of nickel with α-benzildioxime is unsuitable for microanalytical purposes, the results being too high. H. W.

Gravimetric Analysis. VI. Estimation of Calcium. VII. Separation of Calcium from Magnesium. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1918, **31**, 187—188, 203, 214—216).—Estimation of calcium as oxalate or carbonate was submitted to critical examination. It is recommended that the precipitation as oxalate should be made from an acetic acid solution in the presence of ammonium chloride; the calcium oxalate should be weighed as such, since ignition to oxide is less trustworthy, especially in the presence of sulphates. If the latter are present, the oxalate always contains sulphate, but the weight is not affected, since the two have practically identical molecular weights. For the separation of calcium from magnesium, the calcium is precipitated as described from an acetic acid solution; the magnesium is subsequently precipitated as ammonium magnesium phosphate and weighed in this form. [See, further, *J. Soc. Chem. Ind.*, 1919, 29A.] W. P. S.

Estimation of Calcium and Magnesium in different Saline Solutions. E. CANALS (*Bull. Soc. chim.*, 1918, [iv], **23**, 422—430).—The simplest and most satisfactory method of estimating calcium is to precipitate it as oxalate in ammoniacal solution and weigh it as oxide. The method of precipitation as

sulphate and weighing as such is also very exact, providing that numerous precautions are taken. [See, further, *J. Soc. Chem. Ind.*, January, 1919]. W. G.

Sensitiveness of the most usual Tests for Copper. A. Wöber (*Osterr. Chem. Zeit.*, [ii], **21**, 105—107; from *Chem. Zentr.*, 1918, ii, 560).—The usual tests for the detection of copper have been investigated with respect to sensitiveness with a view to their application in microanalysis; the results are given in the form of a table. H. W.

Separation of Hydroxides in the Ammonium Sulphide Group. W. D. Treadwell (*Schweiz. Chem. Zeit.*, 1918, **2**, 59—61, 71—74; from *Chem. Zentr.*, 1918, ii, 663—664).—The separation of bivalent from tervalent metals of the ammonium sulphide group by simple precipitation with dilute ammonia from solutions containing ammonium salts is generally not quantitative. Transitory local excess of the reagent cannot be avoided, and the precipitate then carries down varying amounts of the bivalent metal. The necessary asymptotic approach to the neutral point can be easily attained by leading a current of dilute ammonia (obtained by blowing air through a saturated solution of ammonium chloride in the presence of calcined magnesia) through the solution. Precipitation by the gas has the advantage that it is possible to approach the neutral point with the necessary caution without correspondingly diluting the solution. In the presence of manganese, ammonia should not be added until neutralisation is complete, since the manganese ion is readily oxidised by air in neutral solution and passes into the precipitate; neutrality to litmus is the farthest possible limit. In the separation of chromium and manganese, the latter is always adsorbed by the chromium hydroxide. The hydroxides of the tervalent metals carry down nickel and cobalt more readily than manganese and zinc. The error can be somewhat diminished by precipitating and filtering the main portion of the sesquioxides in distinctly acid solution, and subsequently precipitating the remainder from the filtrate after fresh addition of ammonium salts. The precipitates contain much more basic sulphate than chloride. Precipitates from solutions containing sulphates are more sandy in character and do not adhere to glass; when washed, they lose the sulphate ion and become slimy.

Mercuric oxide is not suitable for the precipitation of the tervalent metals of the ammonium sulphide group as hydroxides. When warmed with dilute ammonium sulphate solution, it only liberates an insufficient quantity of ammonia; addition of ammonium chloride effects an improvement, due to the formation of complex mercury salts. The precipitates are very easily filtered; they are ignited wet, when the admixed mercury compounds are quantitatively volatilised.

For the precipitation of aluminium, chromium, and iron, a

freshly prepared mixture of sodium or potassium nitrite and ammonium chloride is to be preferred to the very unstable ammonium nitrite. The precipitates obtained from solutions of ferric salts by this process are very difficult to filter, and are greatly contaminated with basic salts. The difficulty may be avoided by displacing the nitrous acid from the solution by a current of inert gas at the temperature of the water-bath. The utility of the method is limited owing to the oxidising action of the nitrous fumes.

A portion of the aluminium remains in solution when a dilute solution of aluminium chloride is precipitated by sodium thiosulphate and boiling is continued until sulphur dioxide is completely expelled; precipitation is still less complete in the case of chromium. H. W.

Arsenite Titrations of Permanganate Solutions. Aloke Bose (*Chem. News*, 1918, **117**, 369—370).—Results of experiments are recorded showing that free nitric acid is not the cause of the abnormally high reducing value of sodium arsenite solution when this is used for the titration of permanganate (compare Ibbotson, A., 1918, ii, 175). The formation of manganic compounds does not seem to be possible. Some complicated reactions may take place during the titration, but it is quite clear, from the results of titrations with ammonium ferrous sulphate solution, that all the manganese is present as permanganate before the titration with arsenite is commenced. [See, further, *J. Soc. Chem. Ind.*, 1919.] W. P. S.

Separation of Germanium from Arsenic by the Distillation of the Chloride in the Presence of a Chromate. Philip E. Browning and Sewell E. Scott (*Amer. J. Sci.*, 1918, [iv], **46**, 663—665).—A modification of a method described previously (A., 1917, ii, 546); chromic acid is used to oxidise the arsenic, and the germanium chloride is then distilled from the hydrochloric acid solution. Five c.c. of 10% potassium dichromate solution are sufficient to oxidise 0·25 gram of arsenious acid. A current of carbon dioxide may be passed through the apparatus during the distillation to facilitate the removal of the germanium chloride. If as little as 0·0005 gram of germanium oxide is present, the distillate yields a white precipitate of germanium sulphide on the addition of hydrogen sulphide. [See, further, *J. Soc. Chem. Ind.*, 1918, 785A.] W. P. S.

The Estimation of Phenol and the Three Isomeric Cresols in Mixtures of these Substances. Harry Medforth Dawson and Christopher Archibald Mountford (T., 1918, **113**, 935—944).

General and Physical Chemistry.

The Optical Behaviour of Water of Crystallisation. Käthe Brieger (*Ann. Physik*, 1918, [iv], **57**, 287—320).—Experiments have been made to compare the reflection intensities of crystals of a number of hydrated salts in the infra-red region, $\lambda = 2{\cdot}5$—$7{\cdot}0\,\mu$, with that of water. The reflection curve for water shows a well-marked maximum intensity at $\lambda = 3{\cdot}07\,\mu$, and very similar maxima are found for hydrated crystals (compare Schaefer and Schubert, A., 1916, ii, 505). Of the nine isomorphous alums examined, eight show two maxima in the intensity curves in place of the single water maximum at $3{\cdot}07\,\mu$, their positions being near $3{\cdot}02\,\mu$ and $3{\cdot}51\,\mu$, but differing slightly in the different alums. The curve for cæsium alum, however, shows a third maximum, and in this respect is abnormal. The water maximum at $\lambda = 6{\cdot}22\,\mu$ also becomes doubled in the case of the alums.

As examples of uniaxial crystals, the hexahydrated nickel sulphate and selenate (tetragonal trapezohedral) were examined. In the case of these salts, the water maximum is shifted only slightly. The intensity of the reflection depends on the position of the optic axis relative to the reflecting surface, the water of crystallisation exhibiting dichroism. Similarly in the case of monoclinic crystals of the magnesium sulphate and zinc–ammonium sulphate groups, the reflection properties are closely related to the optical properties, the water being trichroic. It is concluded that the symmetry properties of the water in hydrated salts correspond with the symmetry of the crystals. The bearing of the results on Werner's theory of the constitution of hydrated salts is discussed.

Preliminary experiments with analcime indicate a shift of the water maximum towards the shorter wave-lengths, whilst in every other case the shift is in the other direction. Further experiments may be expected to throw light on the constitution of the zeolites generally, especially with regard to the state of combination of the water which they contain. E. H. R.

Effect of the Electric Field on Spectrum Lines. VII. The Fowler Helium Series. J. Stark, O. Hardtke, and G. Liebert (*Ann. Physik*, 1918, [iv], **56**, 569—576. Compare Fowler, A., 1913, ii, 811).—The effect of an electric field on the lines $\lambda\,3203$ and $\lambda\,2733$ of the Fowler helium series has been studied. The effect is compared with that on the Balmer hydrogen series, and it is shown that both effects are very similar, the lines in both cases being symmetrically resolved into their components. The intensity of the two components is equal. J. F. S.

Effect of an Electric Field on Spectrum Lines. VIII. New Principal Series of Helium Lines which Appear in the Electric Field. J. Stark (*Ann. Physik*, 1918, [iv], **56**, 577—588. See preceding abstract).—During an investigation of the influence of an electric field on the helium spectrum, two new

principal series of lines were discovered. The lines of the first of these, the He *I* principal diffused series, are given by the formula $\nu = Ez(h) - Lz(m,d)$. In the electric field, the lines of this series are resolved in such a way that the components do not lie symmetrically, but are displaced about 1 Å. unit in the direction of shorter wave-lengths. The second new series of helium lines, the He *I* sharp series, is represented by the formula $\nu = Ez(h) - Lz(m,s)$. The lines of this series in an electric field were not resolved into several components, but were displaced towards the longer wave-lengths. The He^+ ion possesses twelve series, which can be arranged in two systems of six series. In each system there are three principal series with the same end-number, and three subsidiary series, also with the same end-number. J. F. S.

Effect of an Electric Field on the Ultra-violet Lines of Helium. G. Liebert (*Ann. Physik*, 1918, [iv], **56**, 589—609. See preceding abstracts).—The ultra-violet lines of the principal series He *I* are displaced towards the red end of the spectrum under the influence of an electric field. Both the components undergo the same amount of displacement. The lines of the second subsidiary series are displaced without resolution toward the red by an electric field. In this case, the displacement is rather more than the proportional amount. The lines of the principal series He *II* are displaced toward shorter wave-lengths by an electric field. In the case of the third subsidiary series of He *I*, a displacement of the lines toward longer wave-lengths is brought about by an electric field. J. F. S.

A New Helium Series under the Influence of an Electric Field. G. Liebert (*Ann. Physik*, 1918, [iv], **56**, 610—616).—Corresponding with the third He *I* series, a subsidiary He *II* series becomes visible in a strong electric field, whereas in a weak electric field it has no noticeable intensity. The electric effect on every member of the principal series corresponds with the effect on the similar member of the subsidiary series. The lines of the subsidiary series, like those of the principal series, are displaced toward the shorter wave-lengths. J. F. S.

Spectrum of the Chromosphere. An Eruptive Protuberance of the 6th July, 1917. P. Carrasco (*Anal. Fis. Quim.*, 1918, **16**, 700—706).—A comparison of the author's observations of the chromosphere spectrum with the results of Rowland and of Adams. The presence of the helium series 6678·1, 4922·1, etc., is noted as a characteristic of the spectrum. The helium series 7665·6, 4713·2, etc., was not observed. W. S. M.

Optical Researches on the Constitution of Sulphurous Acid, its Salts and Esters. Konr. Schaefer [with Willy Köhler] (*Zeitsch. anorg. Chem.*, 1918, **104**, 212—250).—Aqueous solutions of sulphur dioxide show an absorption band in the ultra-violet in the same position as the band given by sulphur dioxide gas, although somewhat broader. Beer's law is not followed, the

band becoming much shallower with increasing dilution. The absorbing substance in aqueous solutions is a hydrate of sulphur dioxide, $SO_2...OH_2$, which appears to be more active than sulphur dioxide itself. Since the normal sulphites and the sulphite esters, $Et{\cdot}SO_2{\cdot}OEt$ and $SO(OEt)_2$, are both transparent in the ultra-violet, it is concluded that sulphurous acid itself is non-absorbing, both in the unionised and ionised condition. The diminished absorbing power of solutions of sulphur dioxide on dilution is attributed to a change of equilibrium from left to right in the equation $SO_2...OH_2 \rightleftharpoons H_2SO_3$. The aqueous solution contains very little sulphurous acid, and it is considered that measurements of the ion concentration in sulphur dioxide solutions have given rise to false ideas regarding the degree of dissociation of sulphurous acid, and consequently of the strength of the acid.

At higher temperatures, solutions of sulphur dioxide absorb more strongly, owing to a shift in the equilibrium of the above equation towards the left. Similarly, addition of sulphuric acid to an aqueous solution of the gas increases the depth of the band in the same manner, but only to a certain limit. When the sulphuric acid exceeds $5N$, the absorption again decreases, probably owing to dehydration, in the sense $SO_2...OH_2 \longrightarrow SO_2 + H_2O$, the free sulphur dioxide being a less strong absorber than its hydrate. In pentane and chloroform solutions, the absorption is similar to that of the free gas, and the solutions follow Beer's law. In solutions of methyl and ethyl alcohols and ethyl ether, the absorption is much increased, and in the case of ethyl ether the band passes into general absorption in the ultra-violet. These solutions also follow Beer's law, and it is concluded that stable compounds of the type $O_2S...OHEt$ and $O_2S...OEt_2$ must be present in such solutions.

Normal sulphites show only end absorption in the extreme ultra-violet, and when a solution of a normal sulphite solution is half neutralised with sulphuric acid, the resulting metal hydrogen sulphite solution at first shows only end absorption, but after a few days, particularly under the influence of light, the sulphur dioxide band develops. When the metal hydrogen sulphite is formed, however, by mixing solutions of sulphur dioxide and normal sulphite, the band is present immediately. A solution of potassium pyrosulphite when freshly prepared shows only end absorption in the extreme ultra-violet, but the band gradually develops. Similarly, sodium methyl sulphite, which in methyl alcohol shows only end absorption, in aqueous solution gradually develops the sulphur dioxide band, more quickly in stronger solutions, owing to hydrolysis into sodium hydrogen sulphite and methyl alcohol.

The equilibrium conditions in aqueous sulphur dioxide solutions are represented by the scheme:

$$SO_2 \rightleftharpoons SO_2...OH_2 \rightleftharpoons \left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}OH\\H\end{matrix}\right] \rightleftharpoons \left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}O\\H\end{matrix}\right]H \rightleftharpoons \left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}O\\H\end{matrix}\right]' + H^{\cdot}$$

$$\left[\begin{matrix}O\\O\end{matrix}S\begin{matrix}O\\H\end{matrix}\right]' \rightleftharpoons \left[OS\begin{matrix}O\\OH\end{matrix}\right]' \rightleftharpoons \left[OS\begin{matrix}O\\O\end{matrix}\right]'H \rightleftharpoons \left[OS\begin{matrix}O\\O\end{matrix}\right]'' + H^{\cdot}.$$

The hydrogen sulphite ion, HSO_3', is probably unstable and undergoes transformation into sulphurous acid and SO_3'', thus: $2HSO_3' = SO_3'' + H_2SO_3$. The sulphurous acid then comes into equilibrium with sulphur dioxide hydrate in the sense $H_2SO_3 \rightleftharpoons SO_2...H_2O$. These changes would explain the gradual development of the absorption band in hydrogen sulphite solutions. The view is expressed that the sulphite ion, $[SO_3]''$, has a symmetrical constitution, and hence also the normal sulphites. This view is supported by the observation that selenious acid and the dialkyl selenites have similar absorption spectra to the normal sulphites (compare A., 1917, ii, 61, 186; 1915, ii, 389). E. H. R.

The Ethylene Chromophore. H. Ley (*Ber.*, 1918, **51**, 1808—1819. Compare Ley, A., 1917, i, 261; Kauffmann, *ebenda*. 391).—The absorption spectra of styrene, stilbene, and cinnamic acid and their derivatives have been studied. Bathochromic effects are produced by the introduction of a methyl, methoxy- or ethoxy-group in the ω-position in styrene, whilst a hypsochromic effect results when the methyl or ethoxy-group is substituted in the α-position; hypsochromic effects are also observed with 7-methylstilbene, β-methylcinnamic acid, β-ethoxycinnamic acid, and α-methylcinnamic acid as compared with the parent substances.

Attempts are also made to connect absorptiometric anomalies with abnormal values for the molecular refraction. The esters of α- and β-methylcinnamic acid are less absorbent than the parent substance and have lower values for the exaltation $\Sigma\alpha$. β-Methylstyrene has an absorption similar to that of styrene, and its refraction anomaly is of the same order. With the hydroxy-derivatives a somewhat similar parallelism is observed, the hypsochromic effect of the ethoxy-group in the α-position corresponding with a distinct diminution of the exaltation. Since, in general, an increase in refractive and dispersive power corresponds with an increase in the unsaturated nature of the compound, the explanation of the "disturbing" action of substituents on the absorption spectra of substances by the assumption of alteration in the degree of unsaturation appears to receive further support.

The extinction-coefficients of chloroform solutions of 1:3:5-trinitrobenzene and styrene, α-ethoxystyrene, β-ethoxystyrene, and β-methoxystyrene respectively have also been measured, but the results scarcely lead to a definite conclusion.

Kauffmann's criticism of the author's views (*loc. cit.*) is reviewed. H. W.

Crystalloluminescence. II. Triboluminescence and Crystalloluminescence. Harry B. Weiser (*J. Physical Chem.*, 1918, **22**, 576—595. Compare A., 1918, ii, 419).—For the further investigation of the relationship between crystalloluminescence and triboluminescence, the phenomena have been studied with crystals of arsenic trioxide and the double sodium–potassium sulphate, $2K_2SO_4,Na_2SO_4$. In each case the colour of the light emitted by the crystals during rapid formation (crystalloluminescence) and that

produced by rubbing or crushing the crystals (triboluminescence) have been determined by photographing through an appropriate series of light filters, and it is shown that the light rays resulting from the two phenomena are identical in colour, that from arsenic trioxide differing considerably, however, from that from the double salt. The colour of the luminescence is therefore a specific property of the compound. The phenomena are held to be chemical in origin. Crystalloluminescence, which is only exhibited by a few inorganic compounds, is due to the rapid re-formation of molecules broken up by the process of electrolytic dissociation. Triboluminescence is due to the re-formation of molecules broken up by the violent disruption of crystals. Whilst all crystalloluminescent substances are also triboluminescent, the reverse is not true. In certain newly-formed crystals a state of strain may exist, and if outside force is applied to such crystals before the internal forces have become adjusted, violent disruption of the crystal may ensue, with consequent molecular decomposition and triboluminescence. The intensity of the triboluminescence depends on the force needed to break up the molecule and the magnitude of the conversion factor for light in the luminescent reaction. E. H. R.

Spectrum of the Ruby and Emera'd. IV. Spectrum Phenomena in the Chromium Compounds. James Moir (*Trans. Roy. Soc. S. Africa*, 1918, **7**, 129—130).—It has been shown previously (*ibid.*, **2**, 321; **3**, 271, 273; **4**, 339) that the almost unique spectra of ruby and emerald are due to chromium oxide which has been compelled to vibrate in an abnormal or constrained manner leading to the production of narrow absorption bands; the constraining substance in the case of the ruby is crystalline alumina and in the case of the emerald it is glucinum silicate. The present communication describes attempts to induce the constrained vibration of ordinary chromium oxide by artificial means. Suitable methods consist in dissolving chromic oxide in concentrated sulphuric acid and gradually adding an organic substance, such as starch, until the orange colour has changed to deep green or, more strikingly, by replacing the sulphuric acid by glacial phosphoric acid. It would appear possible to get a very close imitation of the emerald spectrum by the latter process, but the ruby spectrum, on the other hand, has not been reproduced except by means of alumina.

Concentrated hydrochloric, nitric, perchloric, formic, acetic, and citric acids did not yield very characteristic results, although a faint, hazy band at λ 6800 was seen in several of these solutions. H. W.

A New Electrometer for the Measurement of Radioactivity. B. Szilard (*Anal. Fis. Quím.*, 1918, **16**, 690—699).—A detailed description of a new improved electrometer of the attracted aluminium needle type especially adapted for radioactive measurements. W. S. M.

Radioactivity of some Canadian Mineral Springs. J. Satterly and R. T. Elworthy (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 17—26).—The water of some sixty mineral

springs has been examined with respect to its content of radium emanation and dissolved radium. Measurements of the rate of flow and temperature of the water are also given, together with the nature of the strata. The emanation content varies from $11{\cdot}2 \times 10^{-12}$ curies per litre to 345×10^{-12} curies. The dissolved radium varies between the merest trace and 46×10^{-12} gram per litre, although in most cases the amount is very small. A tabular comparison is given between the factors for these springs and those of American and European springs. Thermal springs are shown to be more active than the cold springs. J. F. S.

The Radioactivity of Mud from Rockanje. E. H. Büchner (*Chem. Weekblad*, 1918, **15**, 243—246).—Examinations of samples of mud from the Waal lake, near Rockanje (A., 1913, ii, 821), showed proportions of radium of the order of 1×10^{-10} parts by weight. Subsequent examination in the following year confirmed this figure. More recent work on samples of the same material by Folmer and Blaauw (A., 1918, ii, 145) indicate a radium content of the order generally found in common rocks and deposits, namely, 1×10^{-12}. The author has examined some of the samples tested by Folmer and Blaauw, and confirms their results. The discordance between the later figures and the earlier results cannot be attributed to differences in the methods of working or to experimental error, but is possibly due to deposition from the river water in isolated places of matter containing a high proportion of some uranium mineral or its degradation products. S. I. L.

The Radioactivity of the Mud from Rockanje. A. H. Blaauw (*Chem. Weekblad*, 1918, **15**, 361—364).—Büchner's arguments (preceding abstract) to account for the differences shown by the later analyses in the radioactivity of the Rockanje deposits are criticised, and the assumptions of patches of higher activity questioned. Other geological arguments suggested by Büchner are shown to be incorrect. It is claimed that the later examination was complete. S. I. L.

Ionisation and Resonance Potential for Electrons in Vapours of Magnesium and Thallium. Paul D. Foote and Fred L. Mohler (*Phil. Mag.*, 1919, [vi], **37**, 33—50).—The ionisation and resonance potentials for electrons in vapours of magnesium and thallium have been measured by the Tate modification of the Franck and Hertz method. The experimental values for magnesium vapour were 2·65 volts and 7·75 volts for the resonance and ionisation potentials respectively. The values calculated from the quantum relation $h\nu = eV$ are 2·70 volts and 7·61 volts respectively. In the case of thallium vapour, the values 1·07 volts and 7·3 volts were obtained for the resonance and ionisation potentials respectively. The theoretical value for the former quantity is 1·07 volts, whilst that of the latter is unknown. The ionisation potential for magnesium is obtained from the limit of

the combination series $1{\cdot}5S - mp_2$, and the resonance potential is determined by the first line in this series, $m=2$. In the case of thallium, the resonance potential is determined by the shorter wave-length member of the first term of the principal series of doublets. No known series in thallium has a convergence frequency greater than 49,263. The observed ionisation potential for thallium suggests the presence of an undiscovered series of single lines converging at $\nu = 1{\cdot}5S = 57{,}000$ to 60,000. The present work offers evidence that the single line spectra of magnesium and thallium are $\lambda = 4571$ and 11,513 Å. respectively. The general behaviour of the metals as regards ionisation and resonance potentials appears to be identical for metals in the same group of the periodic table. In the case of thallium, the component of the doublet having the higher frequency determines the value of the energy quantum absorbed by the atom. This fact suggests either the possibility of separate excitation of the components of a doublet by electronic impact or a behaviour of thallium vapour, thus excited, analogous to the emission of characteristic X-rays, for which the K group does not appear until the energy of the impacting electrons is greater than that corresponding with K_γ. The authors have obtained a value of Planck's constant, h, by the method of ionisation and resonance potentials. Using thirteen determinations on seven different metals, the final mean value $h = 6{\cdot}55 \times 10^{-27}$ erg. sec. was obtained, which is in excellent agreement with recent determinations by other methods. The question of photoelectric sensibility of metallic vapours has been briefly discussed, and recent work on ionisation and resonance potentials has been considered critically. J. F. S.

The Emission of Positive Electricity by Salts of the Alkalies and Alkaline Earths under the Influence of Canal Rays. W. Völker (*Ann. Physik*, 1918, [iv], **57**, 257—277).—It is shown that when a suitably prepared thin layer of lithium chloride or of calcium sulphate, connected with a conducting system, is subjected to bombardment by canal rays, the induced currents can only be explained on the assumption that, when the cathode fall of potential exceeds a certain limiting value, positive charges are emitted by the salt. The limiting value of the cathode fall in the case of lithium chloride is about 500 volts, and with calcium sulphate about 1500 volts. These values correspond with the limiting values found by Stark and Wendt (A., 1912, ii, 720), above which these salts, under the influence of canal rays, emit the characteristic metallic series lines. It is concluded that the carriers which emit the series lines, which are only observed in the space immediately adjacent to the salt, are the positive ions of the metallic elements themselves. E. H. R.

Measurement of Concentration of Hydrogen Ions and a New Form of Calomel Electrode. W. Sturm (*Chem. Weekblad*, 1918, **15**, 912—916).—The author has designed a

hydrogen electrode which reaches equilibrium in about five minutes. This consists of a flask fitted with a rubber stopper pierced with three holes. The electrode, which passes through one of the holes, consists of a glass tube open at its lower end, and is surrounded by a cylinder of platinum gauze. An inner tube carries a copper wire connected to the platinum gauze by means of mercury, and a platinum wire. Hydrogen enters through a tube in the second hole, passes up the electrode, and escapes through a side-tube. The third opening carries a thermometer. The arrangement has the advantage that the fluid is throughout agitated in contact with the hydrogen, which results in a rapid equilibrium. The disadvantage, however, is that a considerable volume of fluid is required. Oxygen is removed from the hydrogen by means of heated platinised asbestos; the presence of small quantities of oxygen must be studiously avoided.

A form of calomel electrode is described in which mercury, mercury–calomel paste, potassium chloride crystals, and saturated potassium chloride solution are employed; such an apparatus has been in use for eight months satisfactorily. S. I. L.

Electrolytic Conductivity in Non-aqueous Solutions. II. Electrical Conductivity of *p*-Tolyltrimethylammonium Iodide in Water and several Organic Solvents. Henry Jermain Maude Creighton and D. Herbert Way (*J. Franklin Inst.*, 1918, **186**, 675—698. Compare *ibid.*, 1916, **182**, 745).—The electrical conductivity of *p*-tolyltrimethylammonium iodide has been determined at 25° in water, methyl alcohol, ethyl alcohol, propaldehyde, anisaldehyde, benzaldehyde, acetone, formic acid, acetic acid, propionitrile, benzonitrile, nitromethane, nitrobenzene, and *epi*chlorohydrin. In the case of some of the solvents, measurements have also been made at 0° and 18° and the temperature coefficient calculated. *p*-Tolyltrimethylammonium iodide, like most strong electrolytes, does not follow Ostwald's dilution law in aqueous solution, but is approximately in agreement with the Storch empirical dilution equation. The ionic conductivity of the *p*-tolyltrimethylammonium ion at 25° in aqueous solution is 40·3. The equivalent conductivity at infinite dilution has been extrapolated for *p*-tolyltrimethylammonium iodide in all the solvents used, and it is shown that the values vary from $\Delta_\infty = 13$ in anisaldehyde to $\Delta_\infty = 188$ in acetone. Further, the magnitude of this value bears a relationship to the chemical constitution of the solvent, which may be generally stated thus: the equivalent conductivity of an electrolyte at infinite dilution, and consequently the velocity of the ions, is greater in an aliphatic solvent than in an aromatic solvent of corresponding constitution. Thus Δ_∞ fo nitromethane = 115, for nitrobenzene 38; for propionitrile 143, whilst for benzonitrile $\Delta_\infty = 54$. In an homologous series, the value for Δ_∞ is greater the nearer the solvent stands to the beginning of the series. For example, Δ_∞ for water = 116, methyl alcohol 100, ethyl alcohol 48, formic acid 90, acetic acid 25. Of

the various substituting groups, the influence of the aldehyde group on the magnitude of Δ_∞ is greatest, whilst that of the carboxyl group is the least, as is shown by the series: acetaldehyde $\Delta_\infty = 188$, nitromethane 115, methyl alcohol 100, acetic acid 25.

J. F. S.

Electrolytic Deposition of Iron from Organic Solvents. E. H. Archibald and L. A. Piguet (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 107—112).—Solutions of ferric chloride in acetone, ethyl alcohol and acetone, and water and acetone, have been electrolysed by various currents and at various voltages at 25°. The experiments were carried out between platinum electrodes, but in some experiments a silver cathode was employed. In all cases, the iron can be completely deposited; in the case of acetone and of acetone–water mixtures, the iron is deposited free from carbon. At low voltages, the iron is deposited in the metallic condition; as the voltage is increased, it comes down as a red deposit which is adherent and allows the iron to be removed from the solution. From the acetone–alcohol solutions, the iron, although completely deposited, is contaminated with carbon. From acetone–water solutions of ferrous sulphate, the iron can be completely deposited, but the deposit contains a considerable amount of carbon. Aldehyde is not formed during the electrolysis of any of the solutions.

J. F. S.

Electrolytic Precipitation of Zinc. D. McIntosh (*Trans. Roy. Soc. Canada*, 1917–18, [iii], **11**, 113—119).—The electrolytic deposition of zinc from solutions of the sulphate has been studied under various conditions with the object of ascertaining the most suitable conditions for obtaining good deposits. It is shown that the best results are obtained when the solution is free from colloids and when the amount of iron present is low. The metals arsenic, antimony, copper, cobalt, nickel, and all metals more electropositive than zinc must be absent. The solution, particularly in tanks containing large amounts of acid, should be cold. The zinc deposits in a semi-passive form; but when it begins to dissolve, solution cannot be stopped in any simple way. The zinc concentration should be as high as possible (6—7%), and no attempt should be made to electrolyse solutions containing less than 1·5—2·0% of zinc. With the ordinary cascade system the maximum current density is 25—30 amperes per sq. foot. A large number of photographs of deposits obtained under varying conditions are reproduced in the paper.

J. F. S.

Critical Phenomena. William R. Fielding (*Chem. News*, 1918, **117**, 379—383).—The relation between the critical pressure and critical temperature of an element can be expressed by the formula $(T_c + 236{\cdot}2)/\sqrt{P_c} = 70{\cdot}9$. This relation holds strictly for hydrogen and the members of the halogen group and less closely for nitrogen and xenon, whilst in the case of oxygen the divergence is considerable. For series of inorganic compounds such as that of the

halogen acids a similar formula holds, $(T_c - x)/\sqrt{P_c} = k$, where x and k are constants for any particular series. In inorganic compounds the critical pressure rises with the critical temperature in any series, but in organic compounds the pressure falls as the temperature rises. For a number of organic compounds the value of $T_c \times \sqrt{P_c}$ has been calculated. In higher members of aliphatic series this quantity tends to become constant. In the aromatic series of hydrocarbons, with the introduction of alkyl groups into the benzene ring, it first decreases, and as the complexity of the alkyl groups increases it becomes practically constant. Multiplication of benzene rings in the molecule produces a considerable increase in the value of the quantity. E. H. R.

Calorimetric Lag. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1858—1872).—Lags may pertain to the thermometer, to various portions of the calorimeter, or to outlying bodies, including air. In this paper the lag of external bodies, such as a thin metal shield surrounding the calorimeter, is treated in a mathematical manner. The effects prove to be three: one, equivalent to a change in the heat capacity of the calorimeter, which can be eliminated by direct calibration of the calorimeter; another, much smaller, depending on the amount of thermal leakage, which can be avoided by using the adiabatic method; and a third, dependent on the jacket temperature, which disappears if this is constant.

On account of the lag effect, the effective heat capacity of a shield midway between calorimeter and jacket is only one-fourth its actual capacity, and, with due regard to the possibility of change, such shields may often be used to reduce thermal leakage. Used as a cover, such a shield has a specially small error, and offers a particularly easy method of dealing with evaporation. (Compare A., 1918, ii, 149.) E. H. R.

The Conditions of Calorimetric Precision. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1872—1886).—In a calibrated calorimeter most of the errors arise in thermometric measurements, and most of these come in the "cooling correction," the determination of the effect of thermal leakage. The leakage effect is equal to $K\phi_x T$, where T is the time, ϕ_x is the difference between calorimeter and environment temperature, and K the leakage modulus of the calorimeter. By diminishing K, as by means of a vacuum, the effect of errors in ϕ_x is diminished. These errors arise from the difficulty in getting the jacket and calorimeter temperatures uniform. The advantage of diminishing ϕ_x, the thermal head, is largely illusory, since the main error, that in determining K by means of the cooling rate, is little affected. Lags, which vary with K and are independent of T and ϕ, can be made to cause little or no error. The rate of stirring should be as uniform as possible, since the heat produced varies as the cube of the speed. The type of stirrer and design of the calorimeter with reference to stirring may be important. E. H. R.

Calorimetric Methods and Devices. WALTER P. WHITE (*J. Amer. Chem. Soc.*, 1918, **40**, 1887—1898).—The general rules for calorimetric precision (preceding abstract) are applied to jacket covers and stirrers and to such special devices as vacuum-jacketed vessels, the adiabatic method, aneroid or dry calorimeters, double or differential calorimeters, and measured-shield calorimeters, and the advantages of the different forms of calorimeter are compared. The measured-shield calorimeter is a new device, having between the calorimeter and the jacket a thin metal shield connected to the wall of the jacket by thermo-elements which are used to measure the thermal head. E. H. R.

Sensitive Bath Thermostat. A. NORMAN SHAW (*Trans. Roy. Soc. Canada*, 1917–18, [iii], **11**, 129—135).—A thermostat on a rather large scale is described which differs but little from the well-known types. A note on the regulation of temperature is appended to the paper. J. F. S.

An Accurate Method for Measuring the Density of Gases. O. MAASS and J. RUSSELL (*J. Amer. Chem. Soc.*, 1918, **40**, 1847—1852).—The method described is applicable to the determination of the density of those gases which can be condensed by liquid air or some other freezing agent. The purified, dry gas is condensed in a suitable vessel, and thence transferred to a large exhausted glass flask (about 2¼ litres capacity) the volume of which is accurately known. The flask has a connection to a manometer, and the pressure is read at 0°, the flask being immersed in ice. By a suitable arrangement of tubes the gas in the flask can be transferred to an exhausted glass bulb immersed in liquid air. When the gas has liquefied, the bulb is sealed off and weighed, and again weighed after it has been opened and the liquid allowed to evaporate. The pressure of the gas remaining in the flask and connecting tubes is read after the bulb has been detached, to enable the volume of gas taken into the bulb to be calculated. The accuracy of the method is limited by the accuracy with which the height of the mercury in the manometer can be read. The probable error with the method used is 0·05%; with the aid of a cathetometer it could be reduced to 0·01%.

The following densities were determined: acetylene, 1·1695; methyl ether, 2·1103; hydrogen bromide, 3·6397. E. H. R.

The Change of Density of Liquid Mixtures with Increasing Temperature. W. HERZ (*Zeitsch. anorg. Chem.*, 1918, **104**, 251—252).—The formula expressing the relationship between density and temperature, $1/d_t = a - b \log(\theta - t)$, where d_t is the density at temperature t, θ is the critical temperature, and a and b are constants, has been found to hold for liquid mixtures as well as for pure liquids. Different binary mixtures of benzene, toluene, aniline, and nitrobenzene were used for the experiments, at temperatures between 25° and 90°, and the differences between observed and calculated densities were very small.

The critical temperature θ of the mixture was calculated from those of the constituents, θ_1 and θ_2, by means of the formula $\theta = n\theta_1 + (100-n)\theta_2/100$, where n and $(100-n)$ are the percentages of each constituent. E. H. R.

Molecular Attraction and Attraction of Mass, and some New Gas Equations. James Kam (*Phil. Mag.*, 1919, [vi], **37**, 65—97).—A theoretical paper, in which gas equations are deduced from considerations of the actual and theoretical co-volumes. A general equation is deduced which considers the effect of temperature on the relation of the co-volumes to the volume. Further reduced isothermals and reduced border-curves are considered. It is shown that the cohesive forces causing the "inward pressure" appear to follow a law similar to the inverse square law of mass attraction. From the deviations from the gas laws a value for the tensile strength of iron is deduced which is of the same order as the experimental value. It is further shown that whatever the ultimate nature of the cohesive forces may be, they seem to be proportional to the square of the molecular weight and to obey the inverse square law—a law consequently similar to Newton's law of attraction of mass. J. F. S.

Internal Molecular Forces of Solid Substances and their Relations with the Elastic Properties. Stefano Pagliani (*Nuovo Cim.*, 1918, [vi], **15**, i, 103—129).—The existence of three forms of internal molecular forces in solids is considered and their values calculated. The first, F, termed intermolecular force of coherence, enters as a factor in the internal work into which thermal or mechanical energy can be transformed without change in the volume of the substance. The second, π, termed internal pressure, is analogous in character to external pressure, and enters as a factor in the internal work in which thermal energy is used with variation of the volume of the substance. The third, called intermolecular force of change of phase, enters as a factor in the internal work accomplished during changes of phase—in the fusion of solids; this force, which acts at the temperature of fusion, where Lindemann considers that the amplitudes of the atomic oscillations about their equilibrium position become of the same order of magnitude as the mean distance between the atoms, appears to be of the same nature as F, which acts with definite values at different temperatures.

The magnitude of the force F exhibits relationships with the values of some of the magnitudes considered in the study and applications of the elastic properties of solids. The simplest of these relations with the moduli of elasticity of tension E, of rigidity n, and of flow N are as follows: $E = 1{\cdot}70\ F$ or approximately $E = 5F/3$, $n = F/\pi$, and $N = 2F/\pi$. The relatively great value of the ratio between E and F depends on the fact that the load E, which should double the initial length of the solid, is only an ideal load unattainable in practice. It is hence more accurate to replace E in technical formulæ by F, this being a real magnitude the value

of which at different temperatures may be calculated by means of physical magnitudes exactly measurable; a number of expressions are given in which this substitution is made. The modulus of elasticity for each species of deformation is found to be directly proportional to the molecular force of coherence. T. H. P.

The Adsorption of Arsenious Acid by Ferric Hydroxide. MAITLAND C. BOSWELL and J. V. DICKSON (*J. Amer. Chem. Soc.*, 1918, **40**, 1793—1801).—The adsorption of arsenious acid from solution, by ferric hydroxide which had been prepared several months previously, has been studied both in presence and absence of sodium hydroxide. The adsorption of the arsenious acid by the ferric hydroxide is diminished by the presence of sodium hydroxide, whilst the adsorption of the sodium hydroxide is itself increased by the presence of the arsenious acid. The age of the ferric hydroxide and the addition of sodium chloride appear not to have any effect on the quantitative data recorded.

The results follow only approximately the "adsorption law," $E=\beta A^p$, where E is the concentration of the adsorbed substance in the adsorbing phase, A its concentration in the solution at equilibrium, and β and p are constants. The equation can be written $\log E = p \log A + B$. Hence if the logarithms of the concentrations in the adsorbent and the solution be plotted, a straight line should be obtained, the slope of which gives the value of p whilst the intercept gives the value of $B=\log \beta$. The curves thus obtained from the results of the authors' experiments approximate to straight lines, but all show a distinct concavity to the x or $\log A$ axis. The adsorption phenomenon cannot be exactly represented by the above equation. The adsorption of arsenious acid by ferric hydroxide was also studied by Mecklenburg (A., 1913, ii, 676), who concluded that the adsorption curves for any particular gel prepared under varying conditions are so related to a unit curve that the ratio of any ordinate on one curve to the corresponding ordinate on the unit curve is a constant. The authors interpret this to mean that the exponent p in the equation $E=\beta A^p$ is constant for any particular gel, whilst β is a variable depending on the conditions of preparation of the gel. The values of p calculated from the authors' and Mecklenburg's results agree when arsenious acid is used alone, but in presence of sodium hydroxide its value increases. E. H. R.

Ferment Action. II. Adsorption of Amino-acids and Polypeptides by Animal Charcoal. Relation of the Observed Appearances to the Cleavage of Polypeptides by Yeast Juice. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1917, **2**, 74—102; from *Chem. Zentr.*, 1918, ii, 738. Compare A., 1917, i, 306).—Animal charcoal adsorbs scarcely a trace of glycine, but it adsorbs a little alanine and a comparatively large quantity of leucine. Similar variations are observed in the case of the polypeptides, even isomeric substances being adsorbed to very different extents by the charcoal. The amount adsorbed at various dilutions

varies according to the laws of adsorption, just as has been observed in the case of enzymes. The adsorptive power of charcoal differs from that of the enzymes, however, in being uninfluenced by changes in the concentration of the hydrogen and hydroxyl ions in the solution.

When mixtures of amino-acids or polypeptides are treated with animal charcoal, the adsorption of the substances containing the more complex molecules is relatively increased, whilst that of smaller molecular substances is decreased. H. W. B.

Ferment Action. III. Adsorption of Amino-acids and Polypeptides and also of various Carbohydrates by Animal Charcoal. EMIL ABDERHALDEN and ANDOR FODOR (*Fermentforsch.*, 1917, **2**, 151—166; from *Chem. Zentr.*, 1918, ii, 739. Compare preceding abstract).—*l*-Arabinose, lævulose, and inositol are less readily adsorbed by charcoal than dextrose, sucrose, and other disaccharides and trisaccharides. The presence of carbohydrates diminishes the adsorptive power of animal charcoal towards polypeptides, and conversely the adsorption of carbohydrates is adversely influenced by polypeptides. H. W. B.

Retardation by Sugars of Diffusion of Acids in Gels. EVARTS A. GRAHAM and HELEN TREDWAY GRAHAM (*J. Amer. Chem. Soc.*, 1918, **40**, 1900—1917).—The rates of diffusion of a number of inorganic and organic acids into gelatin solutions containing varying amounts of dextrose, sucrose, and lactose have been measured. All the sugars have a marked retarding influence on the diffusion of any acid, the disaccharides having a considerably greater effect than the monosaccharide. In agreement with the general diffusion law, the ratio of the distance of diffusion to the square root of the time is found to be a constant in gelatin both with and without sugar. The retardation is not proportional to the concentration of the sugar, but is relatively greater for smaller concentrations of sugar. If the ratio $d/\sqrt{t}$ is equal to K_0 without sugar and K with sugar, the relative retardation is given by $(K_0-K)/K_0$ or Δ/K_0. The relation between concentration of sugar and retardation can be expressed approximately by the equation $(\Delta/K_0)^n=ac$, where c is the concentration and a and n are constants. In 10% gelatin, nitric acid behaves abnormally in that the ratio $d/\sqrt{t}$ is not constant, but increases rapidly at first and, after remaining constant for some time, again decreases. Hydrochloric acid shows the same behaviour in 3% gelatin.

Sodium chloride also retards the diffusion of acids into gelatin, but to a less extent than the sugars when equimolecular solutions are compared. This is the reverse of their effect in reducing the acid swelling of gelatin, in which sodium chloride is more effective than sugar. The physiological bearing of the results obtained is briefly discussed, particularly with reference to the protective action of dextrose in cases of chloroform poisoning, the effects of

which are ascribed to the presence of free hydrochloric acid in the substance. The mechanism of the retardation is also discussed.

E. H. R.

Chemical Affinity in Crystals and the Velocity of Crystallisation. M. Padoa (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 59—64; *Gazzetta*, 1918, **48**, ii, 139—147).—The suggestion is made that, in most cases, crystallisation represents a transposition effected by means of valencies among the more or less free molecules of the gaseous or liquid phase, so that velocity of crystallisation may be regarded as velocity of reaction. The author has measured the velocities of crystallisation of a number of supercooled compounds with the object of ascertaining: (1) if, with isomorphous compounds of similar structure, the velocities of crystallisation are equal or of the same order of magnitude, and (2) if, in a series of compounds of perfectly analogous chemical constitutions, the velocities of crystallisation are comparable and, *ceteris paribus*, dependent on the molecular weights. Similar values are obtained for *m*-bromo- (600) and *m*-chloro-nitrobenzene (882), and also for *p*-dichloro- (4800), *p*-dibromo- (7000), and *p*-iodo-benzene (6000), the low value for *p*-chloroiodobenzene (1153) being apparently dependent on its markedly different viscosity. The introduction of methyl into the benzene ring greatly retards the crystallisation; naphthalene and its analogues show far lower values than benzene, the isomeric anthracene and phenanthrene having identical velocities. Similarity also exists between the velocities for isomorphous inorganic compounds.

Of two compounds of similar structure, the one saturated and the other unsaturated, the latter should present the greater velocity of crystallisation, since the latent affinities in the double linkings should favour the process of crystallisation. This conclusion is completely confirmed by the results obtained for a number of pairs of isomorphous organic compounds, one member of each pair being saturated or at least less unsaturated than the other member.

The general conclusions drawn are: (1) the velocity of crystallisation is a constitutive property, and (2) the bonds between the atoms in crystalline networks are of the same nature as chemical valencies.

T. H. P.

Point of Transformation between Reversible Modifications. C. Viola (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 107—112).—The author applies the law of maximum work and Curie's law to the consideration of the possible co-existence, at a temperature different from T, of two reversible crystalline modifications which occur in contact in stable equilibrium at temperature T and at a definite pressure. It is shown that, either where a process is effected reversibly and crystallisation takes place and should take place according to Curie's law, or where between two modifications in contact a minimal surface tension is established, a point of

transformation must always exist there; vice versa, the surface tension is a minimum at a transformation point between two modifications. T. H. P.

The Artificial Coloration of Liquid Crystals. Paul Gaubert (*Compt. rend.*, 1918, **167**, 1073—1075).—Indophenol may be satisfactorily used for colouring liquid crystals and also solid crystals of a large number of organic compounds. The presence of the indophenol lowers the solidification point of the molten substances, and in the case of substances giving several birefringent liquid phases, all the melting points or transformation points are lowered. There exists for the indophenol a coefficient of solubility particular to each phase, this coefficient diminishing with the molecular volume.

The optically positive liquid crystals obtained by combining cholesterol with glycollic acid, glycerol, etc., are not coloured by indophenol, although the isotropic liquid dissolves it. W. G.

Theory of the Velocity of Coagulation. H. Freundlich (*Kolloid Zeitsch.*, 1918, **23**, 163—173).—A theoretical paper in which it is shown that the velocity of slow coagulation of hydrophobe sols increases very much with increasing concentration of the coagulating electrolyte, whilst for rapidly coagulating sols the velocity of coagulation is constant and independent of the nature and concentration of the electrolyte. Smoluchowski explains the rapid coagulation by assuming that the collisions between the particles are non-elastic and lead to the coagulation of all the particles which come within the sphere of influence. The rapid increase in velocity of the slow coagulation is explained by the assumption that in the concentration present the charges on the particles produce a repulsion, and only those particles are coagulated the kinetic energy of which is greater than a certain critical value. This critical value is greater the greater the charge on the particle. The number of these particles increases as the electrolyte concentration increases. A formula giving the relationship between electrolyte concentration and velocity of coagulation is given, and this is in keeping with observed results. J. F. S.

The Brownian Movement and the Coagulation of Colloidal Solutions. H. W. Woudstra (*Chem. Weekblad*, 1918, **15**, 679—680).—The author claims priority over Kruyt and van der Spek (A., 1917, ii, 563) in directing attention to the function of the Brownian movement of the colloid particles in the coagulation of a colloidal solution. W. S. M.

The Brownian Movement in Relation to the Mechanism of Flocculation. D. J. Hissink (*Chem. Weekblad*, 1919, **16**, 20—21).—The author disputes the contention of Henri and Ostwald (see "Grundriss der allgemeinen Chemie," 1917, 544) that the Brownian movements are diminished by addition of a coagu-

lating electrolyte before coagulation, and contends that by microscopic observation it can easily be seen that the coagulation itself is the cause of the diminution of the movement, which is therefore a consequence of the coagulation and does not precede it.

S. I. L.

The Lowering of the Degree of Dissociation. R. N. DE HAAS (*Chem. Weekblad*, 1918, **15**, 1352—1355).—An elementary mathematical consideration of the fundamental equation of mass action with reference to the shifting of the equilibrium consequent on the addition of one of the products of dissociation or ionisation to the system. W. S. M.

Heterogeneous Equilibria between Aqueous and Metallic Solutions: The Interaction of Mixed Salt Solutions and Liquid Amalgams. V. A Study of the Ionisation Relations of Potassium and Strontium Chlorides in Mixtures. G. McP. SMITH and EDWIN ARTHUR REES (*J. Amer. Chem. Soc.*, 1918, **40**, 1802—1847).—To study the equilibrium between mixed strontium and potassium amalgams and the mixed aqueous solutions of the chlorides of these metals, a definite quantity of either strontium amalgam or potassium amalgam of known concentration was shaken up with successive portions of a known aqueous solution of the mixed chlorides until equilibrium was reached. The quantities of strontium and potassium in the amalgam were then determined by analysis. Experiments were made on the effect of varying (1) the amalgam concentration up to about 0·6 milli-equivalent of potassium or strontium per 10 grams of mercury, (2) the total salt concentration in the aqueous phase from 0·05N to 3N, (3) the ratio of the two salts in the aqueous phase at different total salt concentrations, and (4) the temperature from 15° to 40°. To interpret the data obtained, the value of the expression $(\mathbf{Sr}_{Hg})(\text{K-salt})^2/(\text{K}_{Hg})^2(\text{Sr-salt})=C_c$ was calculated, in which $(\mathbf{Sr}_{Hg})$ and (K_{Hg}) are the respective atom-fractions in the mercurial phase, and (K-salt) and (Sr-salt) are the mol-fractions in the aqueous phase (compare A., 1917, ii, 247). The value of the "equilibrium expression" C_c increases proportionately with the total concentration in the mercurial phase up to 0·3 milli-equivalent per 10 grams of mercury, at temperatures from 15—45°. When the amalgam concentration is kept constant and the concentration of the aqueous phase increased, the proportions of the two salts being kept constant, the value of C_c first falls rapidly as the concentration rises to about 0·4N, but with stronger solutions it approaches a constant value.

Assuming that, in the most dilute solutions examined, 0·05N, an equimolecular mixture of the two salts is completely ionised, it is shown that, as the concentration in the aqueous phase is increased, but the salt ratio kept constant, the proportion of K^+ ions to Sr^{++} ions increases rapidly; also when the ratio of

potassium chloride to strontium chloride is increased, the proportion of K^+ ions increases at a greater rate.

The results obtained at different temperatures have been used to calculate the heat of reaction accompanying the changes between 15° and 40°. With rising temperature, the reaction is exothermic, and the heat of reaction is found to decrease with increasing total salt concentration.

As regards the dissociation of potassium and strontium amalgams, it is shown that the ordinary mass-action expression holds good for mixtures of the two up to a total concentration of about 2 milli-equivalents per 100 grams of mercury. There is evidence of the formation in the aqueous salt mixture of molecular complexes and complex ions, the results being in harmony with Werner's views. E. H. R.

Influence of Substitution of the Components of Binary Equilibria in Solution. XIII. The Solution Equilibria of the Three Isomeric Phenylenediamines with Phenols and the Dinitro-derivatives of Benzene respectively. Robert Kremann and Wolfgang Strohschneider (*Monatsh.*, 1918, **39**, 505—570. Compare this vol., ii, 15).—Melting-point and cooling curves have been obtained for the six binary systems made up of the three phenylenediamines with either α-naphthol or β-naphthol, for the four binary systems composed of α- or β-naphthol with α- or β-naphthylamine, for the system β-naphthol and *p*-toluidine, for the nine binary systems composed of one of the three diphenylamines with one of the three dihydroxybenzenes, for the three binary systems composed of 2:4-dinitrotoluene with each of the phenylenediamines, and for the nine binary systems composed of one of the three phenylenediamines with one of the dinitrobenzenes. The results are given in curves and in voluminous tables. It is shown that *p*-phenylenediamine forms compounds with two molecules of α-naphthol (m. p. 110°) and with two molecules of β-naphthol (m. p. 150·5°). One molecule of *m*-phenylenediamine forms compounds with two molecules of β-naphthol (m. p. 114°) and with one molecule of α-naphthol (m. p. 35°). One molecule of *o*-phenylenediamine forms compounds with one molecule of α-naphthol (m. p. 60°) and with one molecule of β-naphthol (m. p. 86°) respectively. α-Naphthol forms two compounds with α-naphthylamine with one and four molecules of the latter to one of the former compound. A compound is formed containing two molecules of β-naphthol to three molecules of α-naphthylamine, but no compounds are formed between α-naphthol and β-naphthylamine; a simple eutectic is produced by these substances at 47°, and contains 56·5% of the last-named component. An equimolecular compound is formed between β-naphthol and *p*-toluidine (m. p. 87·5°). Equimolecular compounds are formed with *m*-phenylenediamine and catechol (m. p. 64·5°), *m*-phenylenediamine and resorcinol (m. p. 79°), *m*-phenylenediamine and quinol (m. p. 127°), with two molecules of catechol and one mole-

cule of *p*-phenylenediamine, with three molecules of catechol and two molecules of *p*-phenylenediamine, and with three molecules of quinol with one molecule of *p*-phenylenediamine. The details of the system *o*-dinitrobenzene–*p*-phenylenediamine have not been worked out, because of a secondary chemical reaction which interferes with the measurements. Compounds are formed between *m*-dinitrobenzene and the three phenylenediamines of the following composition: (i) three molecules of the nitro-compound with two molecules of *o*-phenylenediamine, (ii) two molecules of the nitro-compound with one molecule of *o*-phenylenediamine, and (iii) one molecule of the nitro-compound with two molecules of *m*-phenylenediamine; no compounds are formed between *p*-phenylenediamine and *m*-dinitrobenzene. In the case of *p*-dinitrobenzene and the three phenylenediamines, compounds are not formed with *o*- and *m*-phenylenediamine, but with *p*-phenylenediamine, a compound of two molecules of the amine and one molecule of the nitro-compound is formed. Full details of the numerous eutectics are given in the paper. J. F. S.

The Dilution Limits of Inflammability of Gaseous Mixtures. III. The Lower Limits of some Mixed Inflammable Gases with Air. IV. The Upper Limits of some Gases, Singly and Mixed, in Air. Hubert Frank Coward, Charles William Carpenter, and William Payman (T., 1919, **115**, 27—36).

The Propagation of Flame through Tubes of Small Diameter. II. William Payman and Richard Vernon Wheeler (T., 1919, **115**, 36—45).

The Inflammation of Mixtures of Ethane and Air in a Closed Vessel. The Effects of Turbulence. Richard Vernon Wheeler (T., 1919, **115**, 81—94).

The Ignition of Explosive Gases by Electric Sparks. John David Morgan (T., 1919, **115**, 94—104).

The Range of Existence of Substances, Kinetic Analysis, and the Estimation of Vapour Pressures from Reaction Velocities. M. Trautz (*Zeitsch. anorg. Chem.*, 1918, **104**, 169—210).—The author distinguishes between the range of stability and the range of existence of any substance. The stability of a substance is dependent on the chemical factors which bring about its formation, and is measured by the energy of the reaction, whilst its range of existence is determined only by the heat of activation needed to bring about its decomposition. The upper limit of existence of a compound is determined by the heat of activation of that binary decomposition which requires the least energy.

From the point of view of the author's theory of reaction velocity (A., 1917, ii, 23; 1918, ii, 151), a large number of reactions are

discussed. The formation of nitrosyl chloride or of nitrosyl bromide is apparently a reaction of the third order, but in all probability is made up of superimposed reactions of lower orders, and formulæ are developed by means of which the higher order reaction can be expressed in terms of reactions of lower orders. On the assumption that nitrosyl chloride formation proceeds in the two stages $NO+Cl_2=NOCl_2$, $NOCl_2+NO=2NOCl$, a method of kinetic analysis is developed which enables the concentration and heat of formation of the intermediate product to be calculated. The heat of formation of $NOCl_2$ is 2500 cal.

The reaction between hydrogen and oxygen in porcelain vessels was supposed by Bodenstein to be of the third order, but the velocity constants do not distinguish between a third- and a second-order reaction. Moreover, probable values for the impact constant are obtained only if it is treated as a second-order reaction. The course of the reaction is probably $H_2+O_2=H_2O_2$ (measurable); $H_2O_2+H_2=2H_2O$ (immeasurably fast). The probable value of the heat of activation for H_2+O_2 is 46,374 cal., and the mean diameter of oxygen and hydrogen molecules, $1{\cdot}62\times10^{-8}$ cm.

The formation of nickel carbonyl from nickel and carbon monoxide, which is apparently a third-order reaction, probably proceeds in the three stages: $Ni+CO=NiCO$ (momentary equilibrium), $NiCO+CO=Ni(CO)_2$ (measurable), and $Ni(CO)_2+2CO=Ni(CO)_4$ (immeasurably fast). It is shown how, from the velocity of the reaction, the vapour pressure of nickel can be calculated, and also its probable boiling point, 3358° *A.T.* The true order of a reaction, for example, in the case of nickel carbonyl formation, can be determined by consideration of the absolute reaction velocity and its temperature coefficient when the mean molecular diameter is assumed.

The velocity of surface reactions is fully discussed, and in this connexion the decomposition of ammonia, phosphine, arsine, and antimony hydride are considered. These reactions are assumed to be of the first order, corresponding with $XH_3 \longrightarrow XH+H_2$ (measurable). The heat of activation in this series decreases with increasing molecular weight. From the heat of activation, the maximum wave-length of the actinic rays which will bring about the decomposition is calculated from the formula

$$q_0=(2{\cdot}843\times10^7)/\lambda.$$

It is concluded that ammonia, phosphine, and arsine should show absorption in the ultra-violet, antimony hydride in the visible spectrum. For ammonia, the maximum wave-length is shown to be 219·6 $\mu\mu$, and in confirmation of this, it is shown experimentally that light of 214—203 $\mu\mu$ is photochemically active towards ammonia.

Other reactions discussed are the formation and decomposition of sulphuryl chloride, the decomposition of sulphur trioxide and hydrogen selenide, the formation of hydrogen sulphide and hydrogen selenide from their elements, and the slow combustion of hydrogen iodide, of phosphorus, sulphur, and carbon. From Rhead

and Wheeler's experiments on the combustion of carbon to carbon monoxide (T., 1912, **101**, 846), assuming that the vapour of carbon is monatomic,, the boiling point of carbon is calculated to be 3542° and its vapour pressure in mm. of mercury at 1100°, $4{\cdot}05 \times 10^{-9}$, the corresponding concentration being $4{\cdot}74 \times 10^{-14}$ mols. per litre.

E. H. R.

Consecutive Reactions. IV. Relationships of the Constants in the Acid Hydrolysis of Esters of Oxalic and Malonic Acids. Anton Skrabal and (Frl.) Danica Mrazek (*Monatsh.*, 1918, **39**, 495—503. Compare A., 1917, ii, 250).—The kinetics of the acid hydrolysis of methyl oxalate, ethyl oxalate, methyl malonate, and ethyl malonate have been studied at 25°. The hydrolysis was effected by 0·1*N*-hydrochloric acid, and since, as has been previously shown, the determination of the change in acidity did not yield a satisfactory constant, the amount of normal ester remaining unchanged was determined iodometrically. In this way, it is shown that the hydrolysis takes place according to the equations for first-order reactions. The ratio of the reaction constants of the two consecutive reactions is 2:1. Methyl oxalate is hydrolysed approximately twice as rapidly as ethyl oxalate, but in the case of the malonic esters, the rate of hydrolysis is approximately the same in the two cases.

J. F. S.

The Conception of the Chemical Element as Enlarged by the Study of Radioactive Change. Frederick Soddy (T., 1919, **115**, 1—26).

Atomic Weights in 1917. E. Moles (*Anal. Fis. Quim.*, 1918, **16**, 625—653).—A review of the work on the determination of atomic weights published during 1917.

Complex Ions. I. M. Kolthoff (*Chem. Weekblad*, 1918, **15**, 1636—1644).—The definitions of complex ions given by de Haas (*ibid.*, 1917, **14**, 752; 1918, **15**, 1352) and Abegg and Bodländer (A., 1899, ii, 542) are criticised. The latter state: "One of the ion-forming components of a complex compound is built up of a single ion with an electrically neutral molecule." de Haas in his later paper defines an inorganic complex ion as "a metal-containing ion built up of one or more molecules and one or more ions." The author does not regard the presence of a neutral molecule as essential. Complex ions arise from the tendency of ions to combine with other molecules or ions, which tendency is the greater the lower is the "electro-affinity" of the ion; the nature of the complex is dependent also on the properties of the molecules or other ions which enter into it. It follows that for any salt, formation of complex ions becomes important only when neutral molecules are present to enter into combination with the ions, that is, when the degree of dissociation is small. Thus salts of strongly electropositive and electronegative ions or groups, and salts of one

strong and one weak radicle, being highly dissociated in solution, show small tendency to complex formation; salts of one strong and one weak radicle or element may, however, form complex ions by combination of the ions of the weaker element or radicle with each other.

The mercuric salts afford numerous examples of the formation of complex ions; dissociation of mercuric chloride forms the ions $HgCl^{\cdot}$, $Hg^{\cdot\cdot}$, and Cl', and combination of the Cl' with the undissociated molecule gives rise to the complexes $HgCl_3'$ and $HgCl_4''$. Of these, the group $HgCl^{\cdot}$ has the highest concentration, namely, about 10,000 times as great as the concentration of the $Hg^{\cdot\cdot}$ ion. A consideration of the possibilities of combination or dissociation of a group $AB^{\cdot}$, where A is a bivalent positive and B a univalent negative ionogen, will show that the neutral molecule AB_2 can be regarded as an intermediate product between the complexes $AB^{\cdot}$ and AB_3'.

The cases of formation of complexes fall into two classes. In the first, the electro-affinity of both ions is great, and the tendency to complex formation small, increasing as the electro-affinity falls. In the case of the chlorides of the alkali metals in solution in presence of an alkaline earth chloride, for example, the lower dissociation of the alkaline earth chloride causes the presence of its neutral molecules, which form complexes with the chlorine ion of the alkali metal chloride, of the type RCl_3'; in concentrated solutions, the product of the concentration of this complex and that of the ion of the alkali metal may be so great as to cause separation of double salts. In the second class, the electro-affinity of both ions is small; it is clear that there will be a gradual transition between the two classes. Silver iodide and mercuric cyanide form examples of slightly soluble salts in this class; here the solubility is greatly increased by presence of either ion, owing to the possibility of complex formation which this introduces. Cadmium iodide affords a good case of a soluble salt of this class.

Consideration is given to complex ions containing hydrogen. For the case of a weak dibasic acid, H_2A, two dissociation constants, corresponding with the ions HA' and A'', have to be considered, the second being usually very small. It is shown that the low dissociation of HA' as compared, for example, with RA', where R is an alkali metal, is in contrast with the case of the halogen acids and the alkali haloids, the former having here the higher dissociation.

The following definition is finally put forward: "Complex ions break up to a certain extent into simple ions, generally with formation of neutral molecules." S. I. L.

The Valency-hypothesis of J. Stark. W. Jacobs (*Chem. Weekblad*, 1918, **15**, 1566—1571).—The theory of partial valencies has been employed to explain molecular aggregation in the fluid and crystalline states and to account for the various states of aggregation in which elements and compounds exist at ordinary

temperatures, and the changes in the states of aggregation which they undergo with change of temperature. The lines of force of a valency-electron can be distributed partly to atoms of the same molecule and partly to other molecules; consequently, intramolecular linking and intermolecular linkings are essentially due to the same forces, and all substances fall within a series in which the relative strength of the two classes of linking gradually changes. If the valency-electron is adjacent to a positive surface within its own molecule, intermolecular attraction will be weak and will be easily overcome by a small inflow of energy from without, which will leave the intramolecular system unchanged; at the other extreme, the strength of the two kinds of linkings approaches equality, the molecule behaves, as it were, like a single atom, and intermolecular aggregation is pronounced. In the last case, any disturbance of the intermolecular linkings must affect strongly the internal arrangement of the single molecules, and it may happen that a particular atomic system can only exist within very narrow limits of physical properties.

Stark has directed attention to the distinction between the meaning of the term molecule in the chemical and in the physical sense; in the former, molecules are distinguished as having identical arrangements of atoms, in the latter as being particles free to move in space in a definite manner determined by thermal conditions. The two definitions agree for molecules in the gaseous condition, since here no intermolecular linkings exist. In the crystalline condition, a chemical molecule is not free to move independently of its neighbours, and the physical definition fails. In the liquid condition, molecular aggregation occurs, but generally varies continually in strength and character; physical molecules exist, but are generally not identical with chemical molecules, being usually built up of several chemical molecules and varying continually in mass. In the case of solution, the molecules of solute by the attraction of their partial valencies form "solution molecules" with molecules of the solvent, each of which is a free-moving physical molecule and changes readily with slight changes of temperature.

Where intramolecular attraction is weak and the electric valency-field is diffused outside the molecule, as in the case of metals and electrolytes, the power of crystallisation is high, and in the liquid condition the substance has low vapour pressure; where the intramolecular linkings are very strong, as with the inert gases, the substance cannot be liquefied or solidified at ordinary temperatures. The gradation of physical properties of the hydrocarbons similarly is explained by the gradual decrease of strength of the intramolecular bonds as the number of similarly linked atoms within the molecule increases. S. I. L.

A Device for Introducing a Vapour into a Gas. E. H. Zeitfuchs (*J. Amer. Chem. Soc.*, 1918, **40**, 1899).—To introduce a known quantity of vapour into a stream of gas, the following

device is used. On to the end of a burette is sealed a glass capillary. This capillary is enclosed by the constricted end of a wide tube, closed at the top just below the cock of the burette by a piece of rubber tubing, which keeps it in position. The capillary touches in the wide tube a roll of asbestos fibres, wound round with resistance wire, by which it is heated electrically. A measured quantity of liquid can be run from the burette on to the asbestos fibre, where it is vaporised and taken up by a stream of gas entering the constricted portion of the tube by a side-tube and passing down through the asbestos roll. Any known quantity of vapour can thus be introduced into the gas. E. H. R.

Stopcock for Dropping Liquids arranged for Equalising the Pressure Above and Below the Outlet in the Stopcock. Harry L. Fisher (*J. Ind. Eng. Chem.*, 1918, **10**, 1014—1015).—An annular groove is provided in the key of the stopcock and a central tube is fitted in the two arms. The groove is in connexion with the outer tube, so that, when the tap is turned off, there is still communication between the atmospheres in the vessels above and below the stopcock. The liquid flows from the upper to the lower vessel through the central tube and the bore of the stopcock. W. P. S.

Inorganic Chemistry.

Recovery of Perchlorate Residues from Potassium Estimations. A. Vürtheim (*Chem. Weekblad*, 1918, **15**, 581—584. Compare A., 1917, ii, 568).—The usual method for the recovery of perchloric acids is to transform all the reagent into its potassium salt, which is easily purified by recrystallisation, and to distil the mixture of this salt with an excess of sulphuric acid in a vacuum. This method allows of recovery of only 25% of the quantity of acid originally used, and, moreover, requires a good vacuum pump. A method has now been devised which consists of the addition of unslaked lime to the collected alcoholic filtrates, filtration and washing of the precipitate with alcohol, and recovery of the mixed perchlorates of calcium, sodium, and magnesium by distilling off the alcohol. The solid residue is warmed in a basin with sufficient 50% sodium carbonate to convert the mixed salts completely into the sodium compound, the whole filtered, and the filtrate concentrated to crystallisation point. A large excess of 40% hydrochloric acid is added, the clear liquid decanted from the precipitated sodium chloride, the last drops being separated on a vacuum filter, and the solution of sodium perchlorate concentrated to D 1·125. A series of determinations carried out with recovered material gave uniformly higher results than duplicate tests carried

out with pure perchloric acid. Investigation showed that the presence of sodium perchlorate in the recovered material diminishes the solubility of the potassium salt, and that therefore more accurate results are obtained by using the recovered material than by working with chemically pure perchloric acid. S. I. L.

Appearance of Fogs in Chemical Reactions. Viktor Rothmund (*Monatsh.*, 1918, **39**, 571—601).—The nature of the fogs produced in certain chemical reactions has been investigated. In the case of the fogs produced when ozone enters into reaction with a large number of reagents (particularly reducing agents), it is shown that the fog consists mainly of water in which a small quantity of the products of the reaction are dissolved. These fogs only occur when the reducing agent is of a volatile nature and when the reaction products are soluble in water. The size of the fog particles is practically the same in a number of very different reactions. The approximate diameter as calculated from the rate of subsidence is 10^{-4} cm. The stability of the liquid drops in saturated water vapour is explained by the increased curvature brought about by the solution of the products of the reaction which effect a reduction of the vapour pressure. In the case of ozone and hydriodic acid, a larger value is calculated for the diameter, and this is explained by the formation of hydrogen peroxide. The ammonium chloride fogs, the fogs from fuming acids, fogs produced by the action of radium emanation on sulphur, carbon disulphide, camphor, and iodine, as well as the electrically produced and atmospheric fogs, are also considered. In all cases, the fog produced shows an analogous behaviour to the ozone fogs and generally has drops of about the same size. J. F. S.

The Waters of the Atlantic Ocean on the Argentine Coasts. Hercules Corti and Héctor H. Alvárez (*Anal. Soc. Quim. Argentina*, 1918, **6**, 108—120).—A detailed study of samples of sea-water taken under varying conditions at different places on the Argentine coast.

Extensive tabular statements are given of chemical composition and of general and physico-chemical properties. The methods of analysis adopted are briefly indicated. W. S. M.

Synthesis of Sulphuryl Chloride in Presence of Organic Compounds. Guido Cusmano (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 201—204).—The keto-cineole described by the author and Linari (A., 1912, i, 272) is similar in many of its chemical properties to camphor, which it may replace in the preparation of sulphuryl chloride from sulphur dioxide and chlorine by Schulze's method. The reaction, $SO_2+Cl_2=SO_2Cl_2$, is also accelerated by *cyclo*hexanone, menthone, or tetrahydrocarvone, but does not occur in presence of *a*-bromocamphor, Reychler's camphorsulphonic acid, camphorquinone, or monobromo- or monochloro-ketocineole (to be described elsewhere) with the halogen attached to the methylene contiguous to the carbonyl group; the reaction is, however,

activated by introducing into the compounds just named a positive radicle, for instance, by transforming the sulphonic acid into either the amide or the anilide, or camphorquinone into the monoxime or *iso*nitrosocamphor. Pernitrosocamphor also catalyses this reaction, but not the anilide of chlorocamphorsulphonic acid. These results are not in disagreement with the view that the catalytic action of camphor is connected with the formation at low temperatures of one or more compounds of sulphur dioxide with camphor.

T. H. P.

New Method for the Synthesis of Ammonia. H. Hampel and R. Steinau (*Chem. Zeit.*, 1918, **42**, 594).—Metallic iron, ammonium chloride, and nitrogen are heated together at 300° under 50 atmospheres pressure. The reaction proceeds according to the equation $3Fe + 6NH_4Cl + 2N = 3FeCl_2 + 8NH_3$. A gaseous mixture is obtained containing up to 99% of ammonia. The portion of this derived from the ammonium chloride may be allowed to react with the ferrous chloride; the ferrous hydroxide formed is reduced and the ammonium chloride recovered for further use. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Mixtures of Nitrogen Peroxide and Nitric Acid. William Robert Bousfield (T., 1919, **115**, 45—55).

Oxidation Pressure Limits (A Theory of the Pressure Limit in Autoxidation). W. P. Jorissen (*Chem. Weekblad*, 1918, **15**, 705—714).—A résumé of the observations and measurements on the lower limit of pressure in the autoxidation of phosphorus in oxygen, and of the theories which have been advanced to account for the facts observed.

The author considers the phenomenon to be a particular case of the ignition of an inflammable gas mixture (phosphorus vapour and oxygen) whenever the ratio of combustible constituent to oxygen becomes sufficiently large, the temperature in this case being sufficiently high to cause spontaneous ignition. W. S. M.

The Atomic Structure of Carborundum determined by *X*-Rays. C. L. Burdick and E. A. Owen (*J. Amer. Chem. Soc.*, 1918, **40**, 1749—1759).—The angle between the edges of the elementary rhombohedron of carborundum, which crystallises in the ditrigonal pyramidal class of the hexagonal system, is 89°56·6′, the departure from the simple cube being due to a shortening by only 0·15% of one trigonal axis of the cube. The results of the *X*-ray measurements here recorded, using rays from a palladium target, show a very close relationship between the crystal structure of carborundum and that of diamond. The silicon and carbon atoms in the carborundum crystal are each arranged on face-centred rhombohedral (nearly cubic) lattices. In the prism planes $(10\bar{1}0)$ and $(11\bar{2}0)$, the carbon and silicon atoms lie in the same planes, from which it follows that in the direction of the principal

axis the carbon and silicon atoms alternate, there being no lateral displacement between the two kinds of atom with respect to this axis. From the relative intensities of the reflections of the spectra of different orders by the different planes, the displacement of the carbon planes from the silicon planes in the direction of the principal axis is calculated to be equal to 0·36 of the distance between two consecutive carbon or silicon planes. The carborundum structure can then be derived from that of the diamond by replacing the carbon atoms of one of the two interpenetrating face-centred cubic lattices of the diamond by a similar lattice of silicon atoms, shortening one trigonal axis by 0·15%, and displacing the atoms of one lattice from a position 0·25 to one 0·36 of the distance between successive planes of the other lattice in the direction of the shortened axis.

From the values of the distances between the atom planes derived from the measurements, the density of carborundum is calculated to be 3·11, the observed value being 3·123. E. H. R.

Electrolysis of Potassium Phosphate. A. Rius y Miró (*Anal. Fis. Quim.*, 1918, **16**, 573—610).—The electrolytic oxidation of potassium phosphates is assumed to take place in two stages, the first being the formation of perphosphate and the second that of monoperphosphate. For dipotassium hydrogen phosphate, the primary reaction can be represented by the equation $2K_2HPO_4 + O = K_4P_2O_8 + H_2O$. The perphosphate then undergoes further oxidation to monoperphosphate, $K_4P_2O_8 + O + H_2O = 2K_2HPO_5$.

A. J. W.

The Fusion of Sodium Hydroxide with some Inorganic Salts. Maitland C. Boswell and J. V. Dickson (*J. Amer. Chem. Soc.*, 1918, **40**, 1773—1779).—When certain salts which can function as oxygen acceptors are fused at high temperatures (300—400°) with sodium hydroxide, the salt is oxidised and hydrogen evolved. Quantitative experiments have been made with sodium arsenite and ferrous sulphate, and it is found that the hydrogen given off is equivalent to the oxygen taken up by the salt. Stannous chloride and vanadium sulphate are also oxidised, and cerous and uranous sulphates to a small extent. It is remarkable that such readily oxidisable salts as sodium nitrite and sodium sulphite are not oxidised when fused with sodium hydroxide. It is perhaps noteworthy that all the bases the salts of which were found to be oxidised belong, with the exception of iron, to groups 4, 5, or 6 of the periodic table.

The mechanism of the reaction consists ultimately in the decomposition of water, the oxygen carrying the oxygen acceptor to a higher stage of oxidation, whilst the hydrogen is evolved as gas. The general oxidising action of water catalysed by sodium hydroxide is also shown by the evolution of hydrogen when such metals as zinc and aluminium are boiled with sodium hydroxide solution.

E. H. R.

Some Properties of Magnesium Ammonium Phosphate and Magnesium Pyrophosphate. Z. KARAOGLANOV and P. DIMITROV (*Zeitsch. anal. Chem.*, 1918, **57**, 353—371).—The conversion of magnesium ammonium phosphate into magnesium pyrophosphate by ignition sometimes is and sometimes is not accompanied by incandescence. The presence or absence of the phenomenon is found to depend on the conditions under which the magnesium ammonium phosphate is precipitated. If precipitated slowly at the boiling temperature, the product does not incandesce, but if formed quickly at lower temperatures, it invariably does, whether precipitated from a magnesium solution or from a phosphoric acid solution. The pyrophosphate formed with incandescence is grey to black in colour, whilst that formed without incandescence is quite white. The authors conclude from their experiments that only samples of magnesium ammonium phosphate which contain traces of organic matter will incandesce on ignition, since when organic matter, such as filter paper, is carefully excluded, no incandescence is observed. There are apparently two modifications of magnesium pyrophosphate, differing considerably in physical properties. The one, formed without incandescence, is loose in texture and white in colour; the other, the formation of which is always accompanied by incandescence, is hard and lava-like, grey to black in colour, and more resistant to hydrochloric and nitric acids. Its colour is due to enclosed particles of carbon, and is only with difficulty removed at a very high temperature by ignition, but can be destroyed by treatment with acids or an oxidising agent, such as ammonium nitrate. The incandescence of any sample of magnesium ammonium phosphate can be prevented by evaporating it before ignition with an ammonium salt or by heating very slowly to the decomposition temperature. The opinion of Balareff (A., 1917, ii, 90) that the properties of the magnesium pyrophosphate obtained depend on the vapour tension (degree of hydration) of the magnesium ammonium phosphate before calcination is shown to be incorrect. E. H. R.

Adsorption of Metals from Drinking Water by Glass. K. SCHERINGA (*Pharm. Weekblad*, 1919, **56**, 8—9).—The proportion of lead in drinking-water can considerably diminish within a few hours. It is known that if an aqueous magenta solution be boiled in a glass vessel, the latter cannot afterwards be cleaned in the ordinary way; this absorption, however, does not occur if the vessel has been previously cleaned carefully with soap and water and afterwards well rinsed out. Since, then, organic dyes are not adsorbed by a cleaned glass surface, it appears very doubtful that metallic salts should be so adsorbed. This conclusion was confirmed by estimating colorimetrically solutions of various salts which had been allowed to remain for two days in carefully cleaned glass vessels. In no case was the slightest diminution of the amount of metal in solution detected. It appears, therefore, that the diminution in the case of lead is due to chemical action, either

by disturbance of an equilibrium when the water is removed from contact with the lead, or by precipitation of finely divided lead carbonate. S. I. L.

Anhydrous Mercuric Fluoride. Otto Ruff and Gustav Bahlau (*Ber.*, 1918, **51**, 1752—1760).—*Anhydrous mercuric fluoride* may be prepared by heating mercurous fluoride in a current of dry chlorine at 275°, or of dry bromine at 400°, or by heating mercurous fluoride at 450° under 10 mm. pressure. Mercuric fluoride forms transparent, octahedral crystals, m. p. 645°; its b. p. is estimated at 650°. It has D^{15} 8·95. Attempts to determine the vapour tension at various temperatures did not yield satisfactory results, since the vessels are attacked by the vapours. The substance is very sensitive to moisture and becomes discoloured by traces of water vapour, which are not analytically demonstrable; on exposure to air, hydrogen fluoride is evolved, and mercuric oxyfluoride and, ultimately, mercuric oxide, remain. With small quantities of water, a white, hydrated oxyfluoride,

$$Hg_3F_4(OH)_2,3H_2O,$$

is formed, whilst with larger quantities, mercuric oxide is gradually produced. Mercuric fluoride dissolves in hydrofluoric acid solution (40%), and, on cautious evaporation, the hydrated fluoride, $HgF_2,2H_2O$, is obtained in small, colourless crystals. The vapours of mercuric fluoride attack platinum above 500°; mixtures of the fluoride with silver, copper, lead, aluminium, magnesium, zinc, tin, chromium, iron, or arsenic react vigorously when strongly heated locally, yielding amalgams and metallic fluorides, the latter being easily isolable in the pure condition if an excess of mercuric fluoride is used. Sulphur tetrafluoride appears to be formed when mercuric fluoride is heated with sulphur, but no reaction occurs with amorphous or graphitic carbon. The fluorine does not appear to be replaced when the fluoride is heated in a stream of chlorine or bromine.

Mercuric chlorofluoride, HgClF, is obtained as a pale yellow substance by passing dry chlorine over mercurous fluoride at 120°; the pale yellow *bromofluoride* is similarly prepared at 105°.

The preparation of mercuric fluoride in quantity is best effected by the process first described. H. W.

Double Catalytic Process in the Oxidation of Aluminium in the Presence of Mercury. Oxidation of Aluminium Powder at the Ordinary Temperature. P. Roncerax (*Bull. Sci. Pharmacol.*, 1918, **25**, 193—198; from *Chem. Zentr.*, 1918, ii, 699).—Aluminium in a fine state of division is oxidised by the air and under water. Pieces of aluminium in contact with iron do not oxidise in water, but in the presence of a small quantity of mercury, aluminium undergoes oxidation through the operation of two catalytic processes. The mercury, owing to the formation of an amalgam, reduces the aluminium to a molecular state, and the mercury oxide produced acts as an agent for the transfer of

oxygen from the air to the aluminium. Pieces of aluminium after rubbing with mercury oxide are rapidly oxidised in the air and under water. H. W. B.

Solubility of Aluminium Hydroxide. E. H. Archibald and Y. Habasian (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 1—6).—The solubility of aluminium hydroxide in ammonia solutions of different concentrations and in similar solutions to which various amounts of ammonium or potassium nitrate had been added, has been determined at 20° and 30°. The method consisted in shaking the freshly precipitated hydroxide in sealed tubes with the solvent for twelve hours in a thermostat, filtering, evaporating measured weights of the solution in a platinum crucible, igniting, and weighing. The following weights of $Al(OH)_3$ dissolve in 100 c.c. of solution of ammonia at 20°:

Normality of NH_4OH, 0·050, 0·100, 0·125, 0·200, 0·500, 1·00.
Grams of $Al(OH)_3$, 0·0070, 0·0080, 0·0250, 0·0380, 0·0450, 0·0240.

The solubility increases, therefore, with the ammonia concentration to a maximum which lies at 0·5*N*-ammonia, and then decreases. In these experiments, it is shown that the amount of aluminium hydroxide in solution after thirty minutes' shaking is considerably more than the above quantity, but decreases as the shaking proceeds until equilibrium is reached, which is always achieved in less than twelve hours. The presence of ammonium nitrate decreases the solubility of aluminium hydroxide in ammonia, and the decrease is greater the higher the temperature and the concentration of ammonium nitrate. The addition of potassium nitrate increases the solubility of aluminium hydroxide to a very marked extent. It is pointed out that in the quantitative estimation of aluminium, only a small excess of ammonia should be used, and a 10% solution of ammonium nitrate should be used in the washing. J. F. S.

Relation between Molecular Structure and the Activity towards Hydrogen Sulphide of Oxide of Iron. G. Weyman (*J. Soc. Chem. Ind.*, 1918, **37**, 333—336T).—Iron oxides obtained by heating at 100° to 650° are equally active as regards absorption of hydrogen sulphide in the cold, but at 750° a change occurs, which may also be effected at lower temperatures by very prolonged heating. It seems that the activity of the oxide is dependent primarily on molecular structure, and not on any particular degree of hydration, but the oxide is derived in almost all cases from some form of hydrate. W. P. S.

Chromatocobaltiammines. Samuel Henry Clifford Briggs (T., 1919, **115**, 67—76).

The Evolution and Oxidation of Chromic Hydroxide in Alkaline Solution. F. Bourion and A. Sénéchal (*Compt. rend.*, 1919, **168**, 59—62).—An alkaline solution of chromic hydroxide

undergoes a change on keeping, which tends to make it lose its chemical activity, particularly in respect to its powers of reducing hydrogen peroxide. This change is the more rapid as the concentration of the chromium is greater and of the alkali is smaller. It is, however, possible to oxidise 97% of the chromium in chrome alum to chromate by adding sodium hydroxide to the solution of the alum containing four times the calculated quantity of hydrogen peroxide, and then immediately destroying the excess of peroxide by shaking the solution with manganese dioxide. W. G.

The Crystalline Structure of Grey Tin. A. J. Bijl and N. H. Kolkmeijer (*Chem. Weekblad*, 1918, **15**, 1264).—A preliminary note on the crystalline structure of grey tin. The authors have shown that the crystals belong to the regular system.
W. S. M.

Bismuth Hydride and Polonium Hydride. Fritz Paneth (*Ber.*, 1918, **51**, 1704—1728).—By application of the methods used in the study of radioactive substances, the author has succeeded in demonstrating that bismuth forms a gaseous hydride which possesses considerable stability at the ordinary temperature and is not decomposed with much greater readiness than antimony hydride; with increasing temperature, the substance rapidly becomes less stable, and is decomposed into its elements at a red heat. The gas can be almost completely condensed by the use of liquid air, and subsequently, in part, regasified.

Bismuth hydride is obtained by the solution of an alloy of magnesium with thorium-*C* or radium-*C* in 0·2*N*-hydrochloric or sulphuric acid. The alloy is prepared by exposing magnesium foil to the radiations of a radiothorium preparation contained in a glass capsule covered with silk paper, which is impermeable to thorium-*X*; shortly after its removal, in consequence of the rapid decay of thorium emanation and thorium-*A*, the deposit consists entirely of thorium-*B* and thorium-*C*. The alloy is placed in a weighing bottle connected with an electroscope in such a manner that a regular current of nitrogen can be sent through the apparatus. After determination of the natural leak of the electroscope, 0·2*N*-hydrochloric acid is dropped on to the alloy; the electroscope soon indicates an activity, which becomes feebler after a few minutes. The results of this and similar experiments show that when magnesium superficially alloyed with bismuth and lead is dissolved in dilute hydrochloric acid, a few thousandths of the bismuth are converted into such a state that they can be carried by a gas current through a cotton wool filter, and that a similar reaction does not occur with lead. A series of control experiments shows that the observed effects are actually due to a volatile compound of bismuth, and not, for example, to the liberation of thorium-*C*, to the selective action of the filter, or to the relatively greater volatility of thorium-*C* chloride.

Polonium hydride is prepared in a similar manner. The alloy

of magnesium and polonium is prepared by the electrolysis of a feebly acid solution of polonium chloride, a piece of magnesium foil being used as cathode. When the alloy is dissolved in dilute acid and the gases evolved are led into an electroscope, an activation is observed which does not decrease in the course of a day, and therefore is caused by polonium. The gas closely resembles bismuth hydride. It is remarkable that a current of oxygen can be used instead of hydrogen or nitrogen for the transport of the gas without sensibly diminishing the yield. The latter is less than in the case of bismuth hydride, and up to the present it has not been found possible to convert more than a few tenths' part per thousand of the polonium into the gaseous state. If the gas current is cooled to $-84°$, the polonium hydride is only partly condensed. The investigation of the gas is rendered very tedious, since in each experiment the electroscope becomes permanently damaged and does not recover when left to itself for a time. H. W.

Bismuth Hydride. II. Fritz Paneth aad Erich Winternitz (*Ber.*, 1918, **51**, 1728—1743).—The application of radioactive methods having shown that bismuth hydride is capable of existence, and having indicated its mode of preparation and general properties (preceding abstract), the authors now describe attempts to prepare it in weighable quantity from non-radioactive material.

The requisite bismuth–magnesium alloy is prepared by heating equal weights of powdered bismuth and magnesium (as free from silicon as possible) in an iron crucible in a rapid stream of dry hydrogen. The alloy is dissolved in approximately 4*N*-hydrochloric or sulphuric acid (or in some cases nitric acid). Bismuth hydride is thus obtained in sufficient quantity to permit its detection either by the formation of a bismuth mirror or by luminescence tests.

The bismuth mirror is obtained in the usual Marsh's apparatus, and very closely resembles the antimony mirror. As generally obtained, it consists of a strong brown ring in front of and a fainter ring behind the heated spot. The former deposit appears to be frequently burnt into the glass and to be unsuitable for further experiments. This drawback can be overcome by placing a pierced clay disk on the tube and allowing the flame to play against this, as also by increasing the velocity of the gas current. The antimony, arsenic, and bismuth mirrors are most readily distinguished by a number of chemical tests involving the use of sodium hypochlorite, yellow ammonium sulphide, hydrogen sulphide, etc., which are fully described in the original. Attempts to estimate the yield of bismuth hydride by weighing the bismuth mirrors show that about 5×10^{-5} of the bismuth used is converted into the hydride, or that the yield is only about one-twentieth of that obtained from thorium-*C*. It should be noted, however, in this connexion that circumstances have prevented the authors from determining the optimum conditions of experimenting.

The authors have also applied Donau's luminescence method (A.,

1913, ii, 743) to the detection of traces of bismuth, and find the procedure very rapid and so sensitive that it is capable of proving the presence of traces of bismuth which cannot be detected by the ring test. For this purpose, the gases issuing from the Marsh's apparatus are ignited, and a piece of pure calcium carbonate is held on a platinum loop in the flame; the bismuth hydride is decomposed, and a portion of the bismuth is deposited on the lime. The latter is allowed to cool, and then placed at the edge of the hydrogen flame, when the presence of bismuth is betrayed by the cornflower-blue luminescence; in similar circumstances, antimony is readily detected by a sky-blue luminescence, both colorations being readily visible in bright daylight.

The absorption of bismuth hydride by various reagents has been examined; the most suitable solution for this purpose appears to be 0·4*N*-silver nitrate solution. Water absorbs the gas to some degree, and 4*N*-sulphuric acid to about the same extent. 0·5*N*-Sodium carbonate solution and *N*-potassium hydroxide solution are more active, whilst the gas is also absorbed by desiccating agents, such as calcium chloride or soda-lime. It is completely decomposed by concentrated sulphuric acid. An aqueous solution of hydrogen sulphide is not more efficient than pure water.

H. W.

Gold Amalgams. N. Parravano (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 168—170; *Gazzetta*, 1918, **48**, ii, 123—128).—Objections are raised to the argument of Guertler (*Metallographie*, 524), who concludes that mercury dissolves in gold, giving origin to a solid solution containing at most about 10% of gold, and that in the amalgams containing 90—0% of gold no other crystalline individual is formed. The author has made the following experiments: (1) Definite quantities of saturated amalgam and of gold are placed in a vessel, and the latter exhausted; distillation of the mercury on to the gold then proceeds until the composition of the amalgam formed reaches that of the solid in equilibrium with the liquid amalgam. (2) A current of hydrogen is passed over the amalgam; the quantity of mercury thus transported will be a function of the tension of the mercury of the amalgam provided that, in any series of experiments, the form of the apparatus and the velocity and duration of the gaseous current are maintained constant. The results show that gold amalgams contain at least the two compounds Au_2Hg_3 and Au_3Hg. T. H. P.

Amalgams. I. Colloidal Gold Amalgam. C. Paal and Hermann Steyer (*Kolloid Zeitsch.*, 1918, **23**, 145—158).—Hydrosols of gold amalgam have been prepared (1) by shaking gold sols with metallic mercury, (2) by allowing a gold sol to remain in contact with metallic mercury at rest, (3) by mixing solutions of gold hydrosol with mercury hydrosol, and (4) by precipitating both gold and mercury from a solution of the mixed chlorides in the presence of a protecting colloid. In the last-named case, amalgam hydrosols

of the composition represented by the formulæ Au_3Hg_2 and Au_2Hg_3 were prepared by reducing a mixture of suitable concentration of the two chlorides in alkaline solution by hydrazine in the presence of the sodium salts of protalbic and lysalbic acids. The solutions after dialysis were evaporated to dryness in a vacuum, and gave brittle substances which possessed a black or greenish-black colour and a metallic lustre. These substances readily dissolved in water with the production of colloidal solutions. The stability, composition, and general properties of the hydrosols varied with the method of preparation. J. F. S.

Solubilities of Ammonium Platinichloride, Platinibromide, and Iridichloride and the Separation of Platinum and Iridium. E. H. Archibald and John W. Kern (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 7—16).—The solubility of the ammonium salts of chloroplatinic, bromoplatinic, and chloroiridic acids has been determined at a series of temperatures in water and in solutions of various strengths of ammonium chloride and ammonium bromide. It is shown that 100 grams of water dissolve 0·2902 gram of ammonium platinichloride at 0·1°, 0·3652 gram at 7·2°, 0·4869 gram at 18·0°, 0·5760 gram at 25·4°, 0·6370 gram at 29·9°, 0·7870 gram at 38·9°, 1·0131 grams at 49·7°, 1·4740 grams at 60·2°, 1·7440 grams at 70·0°, 2·1800 grams at 80·2°, 2·6150 grams at 90·0°, and 3·2515 grams at 99°. Ammonium platinibromide is somewhat more soluble in water than the foregoing salt; 100 grams of water dissolve 0·4165 gram at 0·2°, 0·5002 gram at 7·3°, 0·6438 gram at 19·0°, 0·7384 gram at 25·0°, 0·8147 gram at 29·7°, 1·0355 grams at 40·0°, 1·2087 grams at 50°, 1·5780 grams at 60·0°, 1·9265 grams at 70·0°, 2·3002 grams at 80·0°, 2·8370 grams at 90°, and 3·5866 grams at 99°. Ammonium iridichloride is much more soluble than either of the platinum compounds; 100 grams of water dissolve 0·5661 gram at 0·2°, 0·7055 gram at 10·0°, 1·0910 grams at 25·0°, 1·2066 grams at 30·0°, 1·5665 grams at 40·0°, 1·9664 grams at 50·0°, 2·4567 grams at 60·0°, and 4·3815 grams at 80·0°. In the presence of ammonium chloride, the solubility of the ammonium salts of chloroplatinic acid and chloroiridic acid is much reduced, but that of the iridichloride is several times as large as that of the platinichloride. Ammonium bromide reduces the solubility of the platinibromide. In all three cases, the reduction in the solubility is proportional to the concentration of the ammonium haloid. The difference in the solubility of ammonium platinichloride and iridichloride furnishes a good method for the complete separation of platinum and iridium. Ammonium platinichloride is appreciably less soluble than potassium platinichloride. J. F. S.

Dehydrogenation of Palladium Hydrogen Hydrosol by Metallic and Colloidal Mercury. C. Paal and Hermann Steyer (*Ber.*, 1918, **51**, 1743—1752).—It has been previously shown (Paal and Hartmann, A., 1918, ii, 303) that palladium

hydrosol gradually loses its catalytic activity in the presence of metallic or colloidal mercury; in the course of experiments on the action of the hydrosol on mixtures of hydrogen and oxygen in the presence of mercury, it was observed that the catalyst speedily became passive and that the gradual slight absorption of hydrogen was preceded by a temporary increase in the volume of the latter. This phenomenon forms the subject of the present communication, in which it is demonstrated that the palladium hydrogen hydrosol is decomposed by mercury with evolution of hydrogen, and that dehydrogenation is effected more rapidly by metallic than by colloidal mercury. Analysis of the residual palladium hydrosol and of the mercury proves that a portion of the palladium has passed into the mercury, and that some of the latter has passed into the hydrosol. The action of colloidal mercury on palladium hydrogen hydrosol only leads to uniform results when care is taken that only the least possible excess of hydrazine is used as reducing agent in the formation of the mercury hydrosol. H. W.

Mineralogical Chemistry.

Mineralogy of the H.B. Mine, Salmo, British Columbia. T. L. Walker (*Toronto Univ. Studies, Geol. Ser.*, No. 10, 1918, reprint, 25 pp.).—The oxidised zinc–lead ores of this mine consist of a mixture of hemimorphite, cerussite, and limonite, and occur as bedded "veins" in metamorphosed limestone, with associated quartzite and schists, and penetrated by dykes of minette. A cave in the mine contains also a number of zinc phosphate minerals forming large stalactitic pillars, which yielded about a hundred tons of ore. These stalactites consist mainly of a core of spencerite with a thin crust of hemimorphite, and between the two, solution cavities containing crystals of hemimorphite (anal. I, deducting 6·66% calcite), spencerite, hopeite, parahopeite (anal. II, D 3·236), and hibbenite. Crystallographic descriptions are given of each of these minerals, except the hibbenite, the existence of which is not confirmed. On the floor of the cave, and partly coating the stalactites, is a deposit of a grey or cream-coloured, non-plastic, zinciferous clay (anal. III), resembling the so-called moresnetite and vanuxemite in composition, but doubtless a mixture of some zinc mineral with clay. The phosphoric acid of these minerals was perhaps derived from the solution of apatite in the surrounding rocks.

	ZnO.	MgO.	Al_2O_3.	Fe_2O_3.	SiO_2.	P_2O_5.	H_2O.	Total.
I.	67·35	—	—	—	25·32	—	7·33	100·00
II.	54·69	—	—	—	—	30·46	15·31	100·46
III.	19·99	3·97	16·07	8·01	39·49	0·26	11·12	98·91

The zinc phosphate minerals now known are the following; they

are all remarkable for their chemical purity, there being a complete absence of elements not shown in the formulæ:

Hopeite..... $Zn_3(PO_4)_2,4H_2O$, orthorhombic
Parahopeite..... $Zn_3(PO_4)_2,4H_2O$, triclinic
Tarbuttite ..... $Zn_3(PO_4)_2,Zn(OH)_2$, triclinic
(A., 1908, ii, 397).
Spencerite ..... $Zn_3(PO_4)_2,Zn(OH)_2,3H_2O$, monoclinic (A., 1916, ii, 629).
Hibbenite..... $2Zn_3(PO_4)_2,Zn(OH)_2,6\frac{1}{2}H_2O$, orthorhombic (A., 1916, ii, 569).

L. J. S.

Examination of the Hot Springs at Banff, Alberta. R. T. Elworthy (*Trans. Roy. Soc. Canada*, 1917—1918, [iii], **11**, 27—33).—An analysis of the water of, and the gases evolved from, the six hot springs at Banff, Alberta, has been carried out. The upper hot spring contains the following amounts of dissolved solids in parts per million of water: 634, SO_4; 10, Cl; 133, HCO_3; 239, Ca; 39·7, Mg; 9·1, alkalis; 31, SiO_2. The total solids amount to 1100 parts per million. Among other metals present are iron, aluminium, manganese, strontium, magnesium, lithium, potassium, and sodium. The gases evolved by the springs contained methane, hydrogen, oxygen, carbon dioxide, nitrogen, helium, and argon. Full analyses are recorded in the paper. These springs are the most radioactive of any yet examined in Canada, the emanation content of the gas being $(1910—2370) \times 10^{-12}$ curies per litre, whilst that of the water is $(221—640) \times 10^{-12}$ curies per litre. The dissolved radium is $(8·5—23·5) \times 10^{-12}$ grams per litre. J. F. S.

The Thermal Mineral Springs of Rio Hondo. Hércules Corti (*Anal. Soc. Quím. Argentina*, 1918, **6**, 215—229).—A detailed account of the medicinal properties and chemical composition of the thermal springs of Río Hondo, in the province of Santiago del Estero in the Argentine. W. S. M.

Analytical Chemistry.

Rational Approximated Atomic Weights for Use in Chemical Analysis. N. Schoorl (*Chem. Weekblad*, 1918, **15**, 547—562; *Zeitsch. anal. Chem.*, 1918, **57**, 209—225).—In ordinary analytical work, it is customary to use for the atomic weights values given to the nearest decimal figure corresponding with the degree of accuracy possible for each determination. In 1904, Erdmann proposed to use atomic weights calculated from hydrogen as unity, since most of the values were very close to whole numbers. Since, however, the atomic weights of one or two of the commonest elements cannot be rounded off to whole numbers without introduction of considerable error, the proposal has found little favour.

The author puts forward the consideration that much more satisfactory values are obtained for analytical purposes by taking account of the fact that, whereas in all accurate atomic weight determinations the weighings are reduced to the proper values for weighing in a vacuum, in analytical work the correction for the weight of air displaced is seldom made. He proposes to use a set of "air atomic weights" obtained from the accepted atomic weights by introducing values based on the air correction. The accepted atomic weight of iodine is, for example, 126·92. Allowing for the difference in specific gravity of iodine and the brass weights generally used in chemical analysis, the volume atom of iodine, namely, 126·92 grams weighed in a vacuum, would weigh in air 126·906 grams. Though the value of this air correction is so small as generally to affect only the third decimal place, it becomes much greater in the cases of carbon, hydrogen, and oxygen, the elements chiefly concerned in organic analysis. The atomic weight of hydrogen is given by the International Committee for 1916 as 1·008. Assuming the atomic volume of hydrogen in combination to be 6, the "air atomic weight" becomes 1·0005, which can without any inaccuracy be given as 1·00 for ordinary purposes. The correction for oxygen, assuming an atomic volume of 6, does not alter the accepted value 16·00, whilst carbon with the accepted atomic weight of 12·005 becomes 11·999, that is, for ordinary purposes 12·00. Similarly, the "air molecular weight" of water becomes 18·00 instead of 18·02 on the basis of the true atomic weights.

The values given in the International table of atomic weights for 1916 have been modified to give the air atomic weights for analytical purposes on the basis of the atomic volumes of the elements. The author devotes many pages to a selection of suitable atomic volumes for each element, basing his calculations on Kopp's law that the atomic volumes are additive. In the case of most of the elements, the values adopted for the atomic volumes are averages of very different figures; the values for cobalt, for example, deduced from the oxide, chloride, bromide, sulphide, and sulphate, respectively, are 7, 9, 2, 1, and 4, the average value, 5, being adopted. As the basis for the calculations for obtaining the atomic volumes of the elements from the specific gravities of their compounds, the following atomic volumes are assumed: O=6, S=16, Cl=15, Br=22, I=31. The atomic volumes of the halogens and of the alkali and alkaline earth metals are taken as approximately half of the values deduced from the atomic weights and the specific gravities.

In order to obtain trustworthy figures for molecular and equivalent weights for ordinary analysis, it is suggested that use may be made of the true molecular volumes of the commoner reagents. The molecular weight of oxalic acid, for example, is 126·058, calculated from the accepted atomic weights. The specific gravity being 1·64, the value to be subtracted to arrive at the "air molecular weight" is 0·076, giving the value for use in volumetric analysis as 125·982. By addition of the air atomic weights given in the

table, the value 125·976 is obtained, which agrees with the figure of 125·982 obtained from the molecular volume better than does the figure 126·058 obtained by addition of the accepted atomic weights. This argument is repeated for the various reagents used in iodine determinations. It is shown, also, that in analysis of organic compounds for the elements, use of the "air atomic weights" would reduce the hydrogen content by nearly 1% of its value, and since in analysis the hydrogen content as a rule is somewhat too high, it is contended that the use of the "air atomic weights" will give more accurate results. S. I. L.

The Importance of Electrical Conductivity in Analytical Chemistry. I. M. KOLTHOFF (*Chem. Weekblad*, 1918, **15**, 889—896).—The determination of conductivity can be employed in a great number of cases as an aid in quantitative analysis, and is very simply and easily carried out. The author has indicated a few cases of the application, leaving to later papers the detailed account and the theoretical discussion. The general cases that arise in volumetric work can be divided into two classes: (1) reactions in which all the ions remain in solution; in this case, the conductivity will generally increase; (2) reactions in which ions disappear. In the second class, the conductivity may (*a*) diminish, (*b*) remain unaltered, (*c*) increase. Suppose a material CD to be added in solution to a solution of AB, and suppose AD to be precipitated as a result of the reaction; the nett result is that in the original solution the B ions remain, whilst the A ions are replaced by C. If the specific conductivity of A is greater than that of C, the conductivity will rise; this occurs, for example, in the neutralisation of a strong acid by a base, the H ion being replaced by the ion of the metal of the base. In the titration of hydrochloric acid by means of sodium hydroxide, for example, the conductivity falls rapidly until all the acid is neutralised; if more alkali be added, the conductivity begins sharply to increase. By plotting the conductivity of the solution against the quantity of alkali is added, the conductivity begins sharply to increase. By neutral point of minimum conductivity The application would be of great use, for example, with a strongly coloured solution for which no colour indicator could be used.

If, in the above cases, the conductivity of A is equal to that of C, which may happen when a precipitate is formed, the conductivity will change very little until the reaction is complete, after which further addition of the second solution causes a rapid increase. Here, also, the measurement can be of importance for analysis, especially where the precipitate forms slowly or is microcrystalline. In the case of neutralisation of weak acids or bases, the conductivity generally increases during the titration, since the slightly dissociated acid is replaced by a highly dissociated salt. Further addition of the base causes a sharp rise in the conductivity, by reason of the presence of the hydroxyl ion. If the values are plotted, the neutral point can easily be determined, and the method

is of wide application in this case, since colour indicators are not available with weak acids and bases.

Further applications are, for example, titration of a weak acid in the presence of a strong acid, determination of the combined alkali in a salt of a weak acid, determination of basic or acidic properties of a substance, as, for example, the acid character of hydrogen peroxide, etc. Similarly, the concentration of an electrolyte can be determined from the conductivity with the help of tables, and determinations of conductivity combined with specific gravities or other physical constants can be used for analysis of a mixture of two electrolytes. In food analysis, also, the determination may be of great use. S. I. L.

The Effect of Dilution in Electro-titrimetric Analyses. Gilbert Arthur Freak (T., 1919, **115**, 55—61).

The Quinone Phenolate Theory of Indicators. Spectrophotometric Study of the End Points and Fading of Phenolsulphophthalein Indicators. Charles L. Brightman J. J. Hopfield, M. R. Meacham, and S. F. Acree (*J. Amer. Chem. Soc.*, 1918, **40**, 1940—1944).—The present communication deals with phenolsulphophthalein and its tetrabromo- and tetranitro-derivatives. It is found that these indicators have a number of properties which make them the best series yet developed. They are twice as deeply coloured as phenolphthalein in alkaline solution and show sharper colour changes. The excess of alkali necessary to produce the end-point of the neutralisation of the indicator does not cause any appreciable fading in either short- or long-time periods in the case of phenolsulphophthalein and its tetrabromo-derivative. The colour of phenolsulphophthalein in phosphate buffer solutions does not fade appreciably even in considerable periods of time.

Standardised stock solutions of phenolsulphophthalein can be kept in an ice-box without appreciable change, or even at ordinary temperatures if care is taken to prevent contamination, and will then show the same absorption index when treated with an excess of alkali at different time periods. Different samples of the same lot of solid phenolsulphophthalein will give the same absorption index when treated with an excess of alkali.

An excess of alkali in solutions of tetranitrophenolsulphophthalein causes a fading of the intense red colour to a light yellow, the time of fading depending on the amount of alkali and other experimental conditions.

Details of the experimental methods are promised in a subsequent paper. H. W.

The Elimination of the Volume of a Precipitate. H. D. Steenbergen (*Chem. Weekblad*, 1918, **15**, 1268—1269).—It is sometimes convenient, in order to avoid the washing of a precipitate, to make the estimation of a soluble constituent of a solu-

tion in presence of the precipitate. This may be done by diluting the mixture to two known volumes and estimating the concentration of the solution in each case. A simple formula involving the concentrations thus found is given for the correction required for the volume occupied by the precipitate. W. S. M.

The Significance of the Electrical Conductivity in the Analysis of Potable Water. I. M. Kolthoff (*Chem. Weekblad*, 1918, **15**, 1160—1183).—The determination of the electrical conductivity has been used by Reichert, Kohlrausch and Holborn, and others as a rapid method for estimating the total solid constituents in ordinary potable waters. For this purpose, a mean equivalent weight and a mean equivalent conductivity are assumed. The author shows how untrustworthy are the results obtained by this method with different types of water. A series of measurements on the conductivity of dilute aqueous solutions of those salts which are ordinarily present in drinking-water, such as sodium hydrogen carbonate, chloride and sulphate, potassium nitrate, calcium chloride and sulphate, magnesium chloride, etc., and of binary mixtures of these, establishes the rule that the degree of dissociation of each salt in the mixed solution is that which corresponds with the total concentration of electrolyte, even in the case where the salts have no common ion. By means of this rule, the author has prepared tables which permit the calculation of the equivalent conductivity of a mixture when the chemical composition of the solution is known. The comparison of the calculated and the measured conductivities of a water affords a check on the chemical analysis. W. S. M.

Chlorometry. Octave Lecomte (*Bull. Sci. Pharmacol*, 1918, **25**, 217—218; from *Chem. Zentr.*, 1918, ii, 762—763).—The author estimates the active chlorine in bleaching powder or in hypochlorites by titrating a known quantity of stannous chloride with *N*/10-potassium permanganate first with and then without the addition of the hypochlorite solution. H. W. B.

Detection of Hydrogen Chloride in Chloroform. D. Vorländer (*Ber. deut. Pharm. Ges.*, 1918, **28**, 385—388).—Neutral chloroform when shaken with a very small quantity of dimethylaminoazobenzene gives a yellow-coloured solution; if the chloroform contains a trace of free hydrochloric acid, the yellow coloration changes to violet-red. Carbon dioxide and anhydrous formic and acetic acids, in chloroform solution, do not give a red coloration with dimethylaminoazobenzene. [See, further, *J. Soc. Chem. Ind.*, 1919, 55A.] W. P. S.

Volumetric Estimation of the Sulphion. R. Howden (*Chem. News*, 1918, **117**, 383).—A rapid, approximate method for the estimation of soluble sulphates of the alkali metals in solution is based on their decomposition by barium carbonate. The solution is shaken with pure precipitated barium carbonate in

presence of phenolphthalein, and standard hydrochloric acid is then run in until the red colour is discharged. The solution is filtered and the titration completed on the filtrate, using methyl-orange as indicator. The addition of acid before filtration appears to be necessary to complete the decomposition of the soluble sulphate by the barium carbonate. [See also *J. Soc. Chem. Ind.*, 1919, 57A.] E. H. R.

Folin's Direct Nesslerisation Method for the Estimation of Nitrogen. LOVELL LANGSTROTH (*J. Biol. Chem.*, 1918, **36**, 377—380).—Accurate results are obtained even when impure sulphuric acid is employed for the digestion provided the necessary corrections are made, the latter being ascertained by control blank experiments (compare Folin and Denis, A., 1916, ii, 573). H. W. B.

Estimation of Phosphorus by the Nephelometric Method. EDWARD B. MEIGS (*J. Biol. Chem.*, 1918, **36**, 335—346).—Accurate estimations of phosphorus by means of the strychnine molybdate reagent (compare Kober and Egerer, A., 1915, ii, 794) can only be obtained by adhering strictly to the prescribed procedure. H. W. B.

Action of Iodine on Hypophosphorous Acid and Phosphorous Acid. Application to the Estimation of Hypophosphites and Phosphites. BOYER and BAUZIL (*J. Pharm. Chim.*, 1918, [vii], **18**, 321—334).—In sulphuric acid solution, iodine oxidises hypophosphorous acid to phosphorous acid according to the equation $H_3PO_2 + I_2 + H_2O = H_3PO_3 + 2HI$. This reaction requires about ten hours for completion. The oxidation proceeds a stage further if the solution is treated with an excess of sodium hydrogen carbonate, the phosphorous acid being then converted into phosphoric acid, $H_3PO_3 + I_2 + H_2O = H_3PO_4 + 2HI$. In this case, two hours' contact is required, and the mixture must be acidified with acetic acid before the excess of iodine added is titrated. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

A Modified Scheibler Apparatus for the Estimation of Carbon Dioxide. M. J. VAN'T KRUYS (*Chem. Weekblad*, 1918, **15**, 870—872).—In order to meet the need for a Scheibler apparatus at the Agricultural Testing Station at Maastricht, and in view of the shortage of rubber in Holland, a modification of the original apparatus has been made. The rubber bag and the three-necked bottle in which this is contained between the reaction flask and the gas-measuring apparatus have been removed. The error which would have been caused had the carbon dioxide evolved been allowed to come into contact with the water in the measuring vessel is obviated by using water saturated with carbon dioxide.

In its modified form, the apparatus is found to give more accurate results than in the original form. S. I. L.

Estimation of Carbon Dioxide in Carbonates. Donald D. Van Slyke (*J. Biol. Chem.*, 1918, **36**, 351—354).—The carbonate, either pulverised or in solution, is placed at the bottom of a test-tube, 20 to 25 mm. in diameter, which is placed in a 250 c.c. suction flask containing an excess of *N*/10-barium hydroxide solution. A rubber stopper carrying a small dropping funnel is inserted into the flask so that the bottom of the funnel dips into the test-tube. The flask is then exhausted to a pressure of 50 mm. or less, and the outlet closed with a screw clamp. An excess of *N*-hydrochloric acid, usually about 5 c.c., is admitted slowly from the funnel. When the rapid evolution of carbon dioxide has ceased, the solutions are both agitated by a rotary motion for three minutes. In the case of most substances, this period is sufficient for the complete transfer of carbon dioxide from the inner tube to the barium hydroxide solution. In the analysis of unashed animal tissues, a longer time is necessary, and in the case of bones, at least two hours should be allowed, the solutions being stirred by rotation occasionally during this period and continuously for three minutes at the end of it.

When the reaction is completed, the vacuum is released, the barium carbonate filtered off, and the filtrate titrated with *N*/10-hydrochloric acid, using phenolphthalein as indicator.

The method appears to be applicable to all carbonates, soluble or insoluble, in the absence of acids, such as hydrogen sulphide, which are highly volatile from aqueous solution. H. W. B.

A Physico-chemical Method of Estimating Alkali Carbonates in the Presence of Alkali Hydroxides. Application to the Analysis of Flue Gases. René Dubrisay, Tripier, and Toquet (*Compt. rend.*, 1919, **168**, 56—59).—If 50 c.c. of various solutions, having the same alkalinity, but containing varying proportions of sodium hydroxide and sodium carbonate, are mixed with 50 grams of phenol, heated until solution is complete, and then allowed to cool, it is found that the temperature at which the solution first becomes turbid is higher as the proportion of sodium carbonate to sodium hydroxide increases. The authors have plotted curves for solutions having, respectively, a total alkalinity of 2*N*, *N*, *N*/2, and *N*/4, showing the relationship of temperature to sodium carbonate present. By means of these, the amount of sodium carbonate in a given solution containing both carbonate and hydroxide may readily be determined by bringing the total alkalinity up to one of the four strengths given above by addition of sodium hydroxide, then proceeding as described above and reading off the amount of sodium carbonate present from the curve.

For the determination of the amount of carbon dioxide present in flue gases, 1 litre of the gas is bubbled through 71·5 c.c. of

$N/4$-sodium hydroxide, and then the above estimation is carried out on the resulting liquid, the amount of carbon dioxide present in the flue gases being readily calculated from the amount of sodium carbonate found in the solution. W. G.

Estimation of Alkali Hydroxide and Alkali Carbonate in Alkali Hypochlorite Solution. M. Philibert (*J. Pharm Chim.*, 1918, [vii], **18**, 260—272).—The total alkalinity is found by treating a portion of the sample with a measured excess of $N/10$-hydrochloric acid and potassium iodide solution, titrating the liberated iodine with thiosulphate solution, then adding potassium iodide–iodate solution, and again titrating the iodine with thiosulphate solution; the latter titration is a measure of the quantity of the added acid which remains uncombined, and the difference corresponds with the alkalinity of the sample. To estimate the free alkali hydroxide, another portion of the solution is treated with a measured quantity of $N/10$-barium hydroxide solution, barium chloride solution is also added, the mixture diluted to a definite volume, filtered, and the alkalinity of the filtrate titrated as described above. The difference between the quantities of free and total alkali gives the amount of alkali carbonate. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Carnot's Method for the Estimation of Potassium Salts. Carolina Etile Spegazzini (*Anal. Soc. Quim. Argentina*, 1918, **6**, 196—209).—Analyses according to the original prescription of Carnot (this Journal, 1877, ii, 921) gave results in every case much too high. The same method as modified by Grandeau and by Fresenius also gave high results.

It is essential in the preparation of the bismuth chloride solution from the subnitrate to give particular attention to the acidity and temperature of the resulting solution, the optimum acidity being determined by precipitation of a known quantity of potassium from $N/10$-solution.

Good results were obtained only with pure dilute solutions of potassium chloride ($N/10$—$N/1$). Nitrate solutions also gave good results, but with sulphate solutions the results were much too low.

With mixtures of potassium chloride and calcium chloride, magnesium chloride, or sodium chloride, the method is satisfactory only when the potassium salt is in excess. W. S. M.

Method for the Estimation of Potassium in Blood. S. W. Clausen (*J. Biol. Chem.*, 1918, **36**, 479—484).—Two c.c. of plasma or 1 c.c. of blood are oxidised by boiling with 5 c.c. of a mixture of sulphuric and nitric acids (1 : 20) for half an hour. The excess of nitric acid is quickly evaporated, and the residual liquid washed into a beaker, rendered alkaline, and then evaporated to dryness. The residue is taken up in glacial acetic acid and the potassium precipitated by sodium cobaltinitrite. The precipitate is collected and then heated with dilute sodium hydroxide, which

changes all the nitrite groups to sodium and potassium nitrite, whilst the cobalt is precipitated as the insoluble hydroxide. The nitrites are then estimated by acidifying with sulphuric acid and titrating with permanganate at 70°.

The method appears to give accurate results. H. W. B.

Gravimetric Analysis. VIII. Separation of Calcium from Magnesium. L. W. Winkler (*Zeitsch. angew. Chem.*, 1918, **31**, 214—216).—The following method was found to be the most trustworthy for the separation of calcium and magnesium. The neutral solution, measuring 100 c.c. and containing not more than 0·1 gram of calcium and 0·05 gram of magnesium, is treated with 3 grams of ammonium chloride and 10 c.c. of *N*/1-acetic acid, then boiled, and 20 c.c. of 2·5% ammonium oxalate solution are added slowly. The precipitated calcium oxalate is collected after twenty-four hours, dried at 100°, and weighed. The magnesium in the filtrate is precipitated and weighed as ammonium magnesium phosphate (compare A., 1918, ii, 455). W. P. S.

Volumetric Estimation of Barium. Thos. Steel (*Analyst*, 1919, **44**, 29).—In the method proposed by Waddell (A., 1918, ii, 407), the use of water saturated with barium chromate is recommended for washing the precipitate of barium chromate. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Estimation of Copper by Means of Potassium Thiocyanate, Potassium Iodide, and Thiosulphate. I. M. Kolthoff (*Chem. Zeit.*, 1918, **42**, 609—610).—The process as described by Bruhns is criticised, and modifications are suggested; trustworthy results are obtained if the copper solution is acidified with sulphuric acid after the potassium iodide has been added. The method may be used for estimating the excess of copper in sugar estimations and for estimating copper in the presence of iron, provided that sodium pyrophosphate is added to inhibit the action of ferric salts. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Estimation of Copper and Sugar. G. Bruhns (*Zeitsch. angew. Chem.*, 1918, **31**, 246).—A reply to Schoorl and Kolthoff's modification of the method described originally by the author (A., 1918, ii, 276). W. P. S.

A Very Exact and Rapid Method for the Estimation of Mercury in the Majority of its Compounds. S. Piña de Rubies (*Anal. Fis. Quim.*, 1918, **16**, 661—689).—The method proposed is a combination of the method of Rose-Finkener and that of Eschka, combining the accuracy of the former with the rapidity of the latter. A critical discussion of both methods with the modifications introduced by Cumming and Macleod, and Biewend and Holloway, is given, together with a bibliography of recent literature on the subject since 1914.

The new method as applied to the analysis of mercury minerals

is as follows. The mineral is mixed intimately with fine iron powder, and is carefully heated in a porcelain crucible into which is closely fitted as a cover a small crucible of gold or silver for the condensation of the volatilised mercury. The cooling of the upper crucible is effected by means of a small bladder of indiarubber which, when distended by a steam of cold water, is in close contact with the whole interior surface. After cooling, the inner crucible is washed with alcohol, and the weight of the condensed mercury film determined. The results obtained by this procedure showed a maximum error of 0·07%.

In the case of more volatile compounds of mercury, organic and inorganic, anhydrous potassium carbonate and barium peroxide, either separately or mixed, are substituted for the iron powder.

When the substance to be analysed contains much moisture, for example, a solution, a weighed quantity is evaporated to dryness in the porcelain crucible after the addition of sodium sulphide, and the mercury is determined as before.

The method is applicable without special modification to the analysis of mercury fulminate and fulminate mixtures.

W. S. M.

Analysis of Aluminium Alloys. A. Travers (*Chim. et Ind.*, 1918, **1**, 708—711).—The alloy is heated with sodium hydroxide solution containing a small quantity of sodium carbonate, and the mixture is filtered. The filtrate contains the zinc and aluminium; the zinc is precipitated as sulphide and estimated acidimetrically after precipitation as ammonium zinc phosphate, whilst the aluminium is estimated by Stock's method. The insoluble portion of the alloy is then dissolved in nitric acid, the solution boiled with the addition of ammonium persulphate, the iron and manganese precipitated with ammonia, the precipitate then dissolved in hydrochloric acid, and the iron titrated with titanium trichloride solution; manganese is estimated in a separate portion of the alloy by the persulphate method. If cobalt and nickel are present, they must be separated as sulphides before the manganese is estimated; cobalt is precipitated by means of β-nitrosonaphthol. The magnesium is estimated in the filtrate from the iron and manganese precipitates, and copper is estimated iodometrically in a separate portion of the sample. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Analysis of Aluminium Alloys and Metallic Aluminium. J. J. Fox, E. W. Skelton, and F. R. Ennos (*J. Soc. Chem. Ind.*, 1918, **37**, 328—333T).—A detailed description is given of methods suitable for the separation of lead, manganese, silicon, copper, tin, iron, zinc, magnesium, and nickel in aluminium and in aluminium alloys containing a low or high proportion of zinc. W. P. S.

Estimation of Molybdenum in Ferromolybdenum. W. Hoepfner and O. Binder (*Chem. Zeit.*, 1918, **42**, 564).—A weighed quantity of about 0·5 gram of the sample is heated with

nitric acid (D 1·2), sulphuric acid is then added, and the heating continued until sulphuric acid fumes are evolved; the solution is diluted to 250 c.c., heated with the addition of a few drops of nitric acid, and the iron precipitated with ammonia. The precipitate is dissolved in sulphuric acid and reprecipitated. The two filtrates, which now contain all the molybdenum, are mixed, treated with 50 c.c. of ammonium sulphide, then acidified with sulphuric acid, and heated. The precipitated molybdenum sulphide is collected and weighed, or it may be converted into molybdic acid by ignition. Traces of impurities may be separated by dissolving the molybdic acid in ammonia. Copper, if present, may be separated as described previously (A., 1918, ii, 372).

W. P. S.

The Precipitation of Zirconium Phosphate. George Steiger (*J. Washington Acad. Sci.*, 1918, **8**, 637—639).—In estimating zirconium in minerals by precipitation as phosphate, the composition of the precipitate approximates more closely to that of normal zirconium phosphate as the acidity of the solution increases. The presence of as much free sulphuric acid as possible is advisable to prevent simultaneous precipitation of iron and titanium phosphates, whilst thorough oxidation with hydrogen peroxide is also necessary to prevent titanium precipitating. At least 3%, and possibly as much as 5%, of free sulphuric acid may be present without interfering with the accuracy of the results. Other phosphates, with the exception of those of the rare earth metals, are readily soluble in the acid solution, and may be separated from the filtrate. [See also *J. Soc. Chem. Ind.*, 1919, February.]

C. A. M.

Analysis of Commercial "Pure" Benzols. F. Butler Jones (*J. Soc. Chem. Ind.*, 1918, **37**, 324—327T).—In a mixture containing benzene, thiophen, toluene, carbon disulphide, and "paraffin," the quantity of carbon disulphide is proportional to the difference between the freezing points of the mixture before and after its removal; similarly, the subsequent removal of the thiophen (by means of basic mercuric sulphate) also results in a difference in the freezing point which is proportional to the amount of substance removed. The residual liquid is a mixture of benzene, toluene, and "paraffin"; the difference between its freezing point and that of pure benzene gives the sum of the amounts of toluene and "paraffin" present; the specific gravity of the liquid in conjunction with the freezing point affords a means of estimating these two constituents. A graph is given for solving the four equations involved.

W. P. S.

Modification of Webster's Test for Trinitrotoluene in Urine. F. Tutin (*Lancet*, 1918, ii, 554; from *Physiol. Abstr.*, 1918, **3**, 452).—The urine is extracted with ether, acidified with mineral acid, and again extracted with ether; in the second extract,

an azoxy-compound from trinitrotoluene gives a violet coloration with alcoholic potassium hydroxide. The modifications now proposed are in part minor ones, such as the number of times extraction is performed, but an important change consists in extracting the final ether extract with dilute sodium carbonate solution; this removes substances which mask the characteristic colour of the Webster reaction. H. W. B.

Estimation of Small Quantities of Ethyl Ether in Ethyl Alcohol. H. E. Cox (*Analyst*, 1919, **44**, 26—27).—The method depends on the fact that alcohol of 99% and upwards distils unchanged; any ethyl ether present passes over in the first fractions, and a mixture of constant boiling point is not formed. The amount of ethyl ether may therefore be estimated from the specific gravity before and after distillation, the specific gravity of the alcohol being taken as that obtained after removal of the ethyl ether. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

The Use of Diastatic Reagents. (II) The Detection of Pyramidone and the Differentiation of the Naphthols. Luciano P. J. Palet (*Anal. Soc. Quim. Argentina*, 1918, **6**, 250—257).—To the solution of pyramidone are added some small pieces of the root of lucerne, which contains oxydases and peroxydases. A violet-blue colour is produced on the root fibres on keeping. The addition of hydrogen peroxide accelerates the appearance of, but does not intensify, the colour. The further addition of α-naphthol immediately produces an intense wine-red colour characteristically different from that produced by β-naphthol. This constitutes a delicate test for the presence of small quantities of α-naphthol in β-naphthol. W. S. M.

Assay and Estimation of Nitroso-β-naphthol. Paul Nicolardot and Lucien Valli-Douau (*Bull. Soc. chim.*, 1918, [iv], **23**, 455—459).—For the assay, 2 grams of the material dried at 35° are dissolved in 120 c.c. of acetone in the cold, diluted to 200 c.c. with water, and 100 c.c. of this solution is titrated with a 1·5% solution of iron alum previously standardised against pure nitroso-β-naphthol, the end-point being shown by means of ammonium thiocyanate as an external indicator.

For an exact estimation, an excess of iron alum is added to the solution prepared as above, and the precipitate formed is left overnight, collected, washed free from iron salts with water, dried at 70°, and weighed. It contains 90·7% of nitroso-β-naphthol. W. G.

Volumetric Estimation of Reducing Sugars. A Simplification of Scales's Method for Titrating the Reduced Copper without Removing it from the Residual Copper Solution. W. Blair Clark (*J. Amer. Chem. Soc.*, 1918, **40**, 1759—1772. Compare A., 1916, ii, 117).—The principle of the

method here described is as follows. The sugar solution to be analysed is boiled under standard conditions with a copper citrate–carbonate solution, and the cuprous oxide dissolved by means of hydrochloric acid. Standard iodine solution is then added to oxidise the cuprous salt, and the excess of iodine titrated by means of sodium thiosulphate. To obtain consistent results, it is necessary to carry out the whole operation under exactly standard conditions. These conditions and the strengths of solutions to be used are indicated for quantities of reducing sugar up to 0·075 gram. It is essential, however, for the worker to standardise his own conditions. The sugar factor of the sodium thiosulphate must be determined on a known sample of reducing sugar, using approximately the same quantity as that to be determined and the same conditions of reduction. The ratio of copper to reducing sugar is approximately constant, the greatest variation occurring with small quantities of sugar.

It was found that sucrose in quantities not exceeding 100 mg. per 10 c.c. and 50% ethyl alcohol do not reduce copper citrate–carbonate solution, but 10% formaldehyde effects a small reduction. [See also *J. Soc. Chem. Ind.*, 1919, February.] E. H. R.

Source of Error in the Use of Picric Acid in Colorimetric Estimations in Biological Fluids. Alice Rohde and Marion Sweeney (*J. Biol. Chem.*, 1918, **36**, 475—477).—It is shown that picric acid which has been preserved in a moist condition for several months loses some of its power of precipitating chromogenic substances in the blood. The use of such picric acid for the estimation of dextrose in the blood by the Benedict-Lewis colorimetric method would yield too high values. H. W. B.

The Colorimetric Estimation of Sugar in the Blood by the Reduction of Picric Acid. C. Salomon (*Biochem. Zeitsch.*, 1918, **90**, 39—52).—As a result of the critical examination of the method of Lewis and Benedict and its modifications, the author arrives at the conclusion that it has considerable value as regards accuracy and speed for clinical investigations. S. B. S.

Estimation of Dextrose in the Blood. F. Hamel (*Bull. Sci. Pharmacol.*, 1918, **25**, 223—224; from *Chem. Zentr.*, 1918, ii, 769).—Ten c.c. of venous blood are treated with 10 c.c. of a 10% solution of trichloracetic acid, and, after removal of the precipitated protein, the dextrose is estimated by Fehling's solution in the usual way. H. W. B.

Estimation of Sugar in Milk and Urine. B. Sjollema (*Chem. Weekblad*, 1918, **15**, 1483—1485).—The method of Folin and Denis (A., 1918, ii, 208) for estimating sugar in milk and urine is recommended. A. J. W.

Estimation of Lactose. E. Hildt (*Compt. rend.*, 1918, **167**, 756—759).—For the determination of lactose in milk in which

the sugar has undergone more or less hydrolysis, the author recommends completing the hydrolysis by means of sulphonic acids, such as those of benzene or phenol or those described by Twitchell (A., 1900, ii, 296), and determining the cupric reducing power. One % solutions of these acids hydrolyse 0·5% solutions of pure lactose in four hours at 100°, but milk serum requires longer heating. No destruction of galactose occurs as when mineral acids are employed. In the determination of reducing power, using 10 c.c. of boiling alkaline copper solution, 0·0506 gram of hydrolysed lactose is equivalent in reducing power to 0·0708 gram of lactose hydrate or 0·0495 gram of invert-sugar.

Considerable destruction of sugar takes place when the solids of milk which has become unsound are dried at 100°; this is attributed to the formation of melanoidins (see Maillard, A., 1912, i, 169) by interaction of sugar and proteolytic products. [See, further, *J. Soc. Chem. Ind.*, 1919, 51A.] J. H. L.

Micro-estimation of Lipoids by Titration. Ivar Bang (*Biochem. Zeitsch.*, 1918, **91**, 86—103).—The fats are oxidised by *N*/10-potassium chromate solution at the ordinary temperature in presence of excess of sulphuric acid. Excess of chromate solution is then estimated by the addition of potassium iodide and the titration of the liberated iodine by thiosulphate solution. The fat (from blood, etc.) is taken up in benzene solution, a little alkali is added (to emulsify the fat), and then the solvent is distilled off. Cholesterol can be estimated in the same manner (and the same factor is used in making the calculations; this factor is determined empirically, as under the conditions of experiment employed, the oxidation is not complete). When cholesterol is present with fats, the determination of both constituents can be made by precipitation of the cholesterol as digitonide, which is insoluble in benzene. When cholesterol esters are present with fats, the determination of the amounts of the constituents can be made in two ways. Either a strength of alkali can be employed which will hydrolyse the fats, but not the cholesterol ester, which can then be separated from the soaps by benzene, or sufficient alkali can be added to saponify both fats and cholesterol esters, and the cholesterol can then be extracted by benzene and estimated separately. In another portion, fats and esters can be estimated together by oxidation. A series of experiments on the oxidation of the lecithides is also described. S. B. S.

The Micro-estimation of the Lipoids of the Blood. Ivar Bang (*Biochem. Zeitsch.*, 1918, **91**, 235—256).—An amplification of the author's micro-method (preceding abstract) is given. Cholesterol and neutral fats are extracted first by a fraction of light petroleum of low boiling point containing chiefly pentane. These can be separated by the method already given, using the digitonin compound of cholesterol. After extraction with petroleum, the blood is extracted with 92% alcohol in the cold. This fraction contains the phosphatide and the cholesterol esters.

S. B. S.

Gravimetric Estimation of Glycyrrhizin. A. Astruc and (Mlle.) G. Pichard (*J. Pharm. Chim.*, 1918, [vii], **18**, 289—290).—Three grams of dry liquorice extract are dissolved in 30 c.c. of water containing five drops of ammonia, the solution is filtered, and 20 c.c. of the filtrate are treated with 2·5 c.c. of sulphuric acid; the precipitated glycyrrhizic acid is collected after twenty-four hours, washed with 30 c.c. of water, then dissolved in ammonia, and the solution evaporated. The residue is dried at 100° and weighed; to the weight obtained is added 0·04 gram as a correction for the solubility of the glycyrrhizic acid in the wash-water. [See, further, *J. Soc. Chem. Ind.*, 1919, February.]

W. P. S.

A New and Delicate Reaction of Pyramidone and its Differentiation from Antipyrine. Luciano P. J. Palet (*Anal. Soc. Quim. Argentina*, 1918, **6**, 151—155).—The author finds that an acid solution of pyramidone when treated with a few drops of an acid solution of potassium ferricyanide and ferric chloride gives an intense blue coloration and precipitate of Prussian-blue. The test is very delicate. With antipyrine, a blood-red colour is obtained with the same reagent. This colour is converted into a pale yellow by the addition of a few drops of hydrochloric acid. The test is therefore carried out in hydrochloric solution, which permits the blue due to the presence of pyramidone in a mixture to emerge. In this way, 1/100 part of pyramidone may be detected in one part of antipyrine.

Phenacetin, acetanilide, aspirin, exalgin, and caffeine give no reaction with the reagent. W. S. M.

The Reaction of the "Ferri-ferric" Reagent with Alkaloids, Glucosides, and other Vegetable Principles. Luciano P. J. Palet (*Anal. Soc. Quim. Argentina*, 1918, **6**, 156—158).—An extension of the application of a mixed solution of potassium ferricyanide and ferric chloride as a reagent (see preceding abstract) to the characterisation of alkaloids, glucosides, and other substances of vegetable origin.

Of 102 substances of this kind tested, 42 gave a positive reaction, that is, a more or less intense blue coloration. W. S. M.

Estimation of Phenacetin and other *p*-Aminophenol Derivatives by Means of Hypochlorous Acid. A. D. Powell (*Analyst*, 1919, **44**, 22—25).—For the estimation of *p*-aminophenol, *p*-phenetidine, etc., the substance is treated with hydrochloric acid and sodium hypochlorite solution, the excess of chlorine is removed by a current of air, potassium iodide is then added, and the liberated iodine titrated with thiosulphate solution. In the first phase of the reaction, *p*-benzoquinonechlorimine is formed; this, after the removal of the excess of chlorine, reacts with hydriodic acid, liberating four atoms of iodine, *p*-aminophenol being re-formed. In the case of phenacetin, a preliminary boiling for two hours with hydrochloric acid is necessary. Each c.c. of *N*/10-thiosulphate

solution is equivalent to 0·00273 gram of *p*-aminophenol, 0·00343 gram of *p*-phenetidine, or 0·00448 gram of phenacetin. [See, further, *J. Soc. Chem. Ind.*, 1919, February.] W. P. S.

Arsenotungstic and Arsenotungstomolybdic Complexes as Reagents for Phenolic Amines. Luis Guglialmelli (*Anal. Soc. Quim. Argentina*, 1918, **6**, 185—195).—Reagents prepared by boiling solutions of sodium tungstate with arsenic acid, and a mixture of sodium tungstate and molybdate with arsenic acid, until concentrated hydrochloric acid no longer produces a precipitate, have been shown to give delicate colour reactions with phenols and some purine derivatives. The same reaction, that is, an intense blue colour, is given by phenolic amines. The author has investigated a large number of substances of this class, and also nitro-, sulphonic, and hydroxy-derivatives of these. Positive results were given with the first reagent with the substances NH_2·OH, NH_2–NH_2, NHR–NH_2, NHR–NHR, NHR–OH, and also with compounds containing the same groups separated from each other, but united directly to a benzene, naphthalene, purine, or pyrazolone nucleus. The second reagent reacts with substances containing the same groups, and, in addition, with substances containing one amino-group, for example, aniline. W. S. M.

Estimation of the Carbamide Fraction in Blood. Heinrich Schur and Franz Urban (*Wien. Klin. Wochenschr.*, 1918, **31**, 892—896; from *Chem. Zentr.*, 1918, ii, 673).—The blood serum is freed from albumin by treatment with sulphosalicylic acid solution (20%); nitrogen is estimated by means of bromine and sodium hydroxide in accordance with the method of Knop and Hüfner. H. W.

Detection of Quinine. Hans Salomon (*Ber. deut. pharm. Ges.*, 1918, **28**, 273—275).—The green coloration obtained when a quinine solution is treated with chlorine and then with ammonia will detect 1 part of quinine in 10,000. The fluorescence observed when a quinine solution is treated with dilute sulphuric acid will detect 1 part of the alkaloid in 200,000 parts. It is advantageous to use bromine-water in place of chlorine in the above test, since it is easier to add just the requisite quantity; the bromine is added until the solution is coloured slightly yellow. Another sensitive reagent for quinine consists of potassium iodide (10 grams), mercuric chloride (2·7 grams), water (200 grams), and glacial acetic acid (2·5 grams). [See, further, *J. Soc. Chem. Ind.*, 1919, 54A.] W. P. S.

Estimation of Quinine in Animal Tissues. W. Ramsden, I. J. Lipkin, and E. Whitley (*Ann. Trop. Med. Parisitol.*, 1918, **12**, 233—258).—See this vol., i, 106.

Estimation of Morphine in Complex Products. I. Revision of the Analytical Reactions Involved. Alfred Tingle (*Amer. J. Pharm.*, 1918, **90**, 689—706).—A discussion of

various methods and reactions used in the estimation of morphine; the acidimetric method and iodometric method (depending on the formation of the periodide) are trustworthy, but the iodoacidimetric method cannot be used. In methods where the morphine is precipitated by ammonia, the presence of alcohol should be avoided. Barium hydroxide solution does not dissolve morphine completely in the presence of lead acetate. The statement in the British Pharmacopœia that morphine tartrate gives the reactions of morphine and of tartrates is substantially correct. [See, further, *J. Soc. Chem. Ind.*, 1919, 27A.] W. P. S.

Estimation of Morphine in Complex Products. II. Mixtures containing Morphine as a Simple Salt. ALFRED TINGLE (*Amer. J. Pharm.*, 1918, **90**, 788—795).—The following method is described for the estimation of morphine in powders, pills, etc., provided that the alkaloid is not present in the form of opium. Six grams of the sample are warmed with 2 grams of calcium carbonate and 20 c.c. of water until disintegrated, 60 c.c. of cold saturated barium hydroxide solution are then added, the mixture is shaken, diluted to 100 c.c., and filtered. Fifty c.c. of the filtrate are treated with dilute sulphuric acid in quantity just sufficient to precipitate the barium, the mixture then diluted to 55 c.c., and filtered. Fifty c.c. of this filtrate are neutralised with sodium hydroxide solution, then rendered slightly acid with hydrochloric acid, evaporated to 5 c.c., and extracted five times with a mixture of chloroform and alcohol (2:1) after the solution has been rendered alkaline by the addition of a slight excess of saturated sodium hydrogen carbonate solution; 25 c.c. of the solvent are used each time. The residue obtained on evaporating the solvent from the extract is titrated with *N*/10-sulphuric acid, using cochineal or lacmoid as indicator. [See, further, *J. Soc. Chem. Ind.*, 1919, 54A.] W. P. S.

Estimation of Tyrosine in Proteins. CARL O. JOHNS and D. BREESE JONES (*J. Biol. Chem.*, 1918, **36**, 319—322).—Tyrosine can be estimated in a protein after hydrolysis with hydrochloric acid by means of the colorimetric method of Folin and Denis (A., 1912, ii, 1012). Tryptophan and hydroxytryptophan are destroyed during the hydrolysis, and their decomposition products, as well as oxyproline, do not give any colour with the Folin-Denis reagent. H. W. B.

New Contact Test for Albumin in Urine. U. P. STEWART (*J. Amer. Med. Assoc.*, 1918, **71**, 1050; from *Physiol. Abstr.*, 1918, **3**, 451).—The reagent is an aqueous solution of picric acid, magnesium sulphate, and citric acid. H. W. B.

General and Physical Chemistry.

Quantitative Spectra of Lithium, Rubidium, Cæsium, and Gold. A. G. G. Leonard and P. Whelan (*Sci. Proc. Roy. Dubl. Soc.*, 1918, **15**, 274—278).—The spark spectra of dilute solutions of the chlorides of lithium, rubidium, cæsium, and gold have been photographed with the object of ascertaining the persistency and intensity of the lines with dilution. The measurements were made with a single prism quartz spectrograph (Hilger). In the case of lithium chloride, the most persistent lines are λλ 6708·2 and 4602·5; these lines persist to a dilution 0·001%, whilst the line λ 6103·8 only persists to 0·01%. The lines of rubidium chloride do not exhibit any remarkable persistency, only one, λ 4571·8, appearing with a 0·1% solution. Solutions of cæsium chloride exhibit a fair number of lines, the most persistent being λλ 4593·5, 4555·5, 4540·2, and 2525·8, these all being visible in a 0·001% solution. The solution lines of gold chloride are not very persistent; no lines are visible in a 0·01% solution; the lines obtained from a 0·1% solution are λλ 4792·8, 4310·7, 3927·8, 3133·2, 3122·9, 2918·5, 2676·1, 2641·6, and 2201·4. J. F. S.

Gamma Ray Activity of Thorium-*D*. Herbert N. McCoy and G. H. Cartledge (*J. Amer. Chem. Soc.*, 1919, **41**, 50—53. See this vol., ii, 120).—Two methods are described for the determination of the γ-ray activity of thorium-*D*. The first consists in measuring the activity of the sulphide in terms of a standard (0·355 mg. radium) and making emanation determinations by the method previously described (*loc. cit.*). The second method consists in sealing radiothorium precipitate in a crystallising dish and comparing with radium in a similar dish. As a mean value of the experiments, it is shown that Th-*D* : Th = $0·956 \times 10^{-7}$. Using the value found by McCoy and Henderson (A., 1918, ii, 422), that 1 gram of radium is equivalent to $8·85 \times 10^{6}$ grams of thorium, it is shown that $1·46 \times 10^{-7}$ grams of radium has the same γ-activity as 1 gram of thorium. Combining the Ms : Th ratio $0·52 \times 10^{-7}$ with the present Th-*D* : Th ratio, the value $1·48 \times 10^{-7}$ is the radium equivalent of the γ-products of thorium determined separately. Thorium-*D* therefore furnishes 1·81 times as much γ-activity as the mesothorium in equilibrium with the same amount of thorium. Taking account of the fact that only 35% of the thorium disintegrates into thorium-*D*, this means that, atom for atom, thorium-*D* contributes 5·17 times as much γ-activity as mesothorium. J. F. S.

Absorption of *X*-Rays. Tycho E:son Aurén (*Phil. Mag.*, 1919, [vi], **37**, 165—207).—Making use of the method previously described (A., 1917, ii, 350), the author has determined the relative

absorption coefficients of a number of elements, including aluminium, iron, nickel, copper, and tin, and of a very large number of inorganic and organic compounds. In the case of the compounds, the additive law has been found valid throughout. With the possible exception of carbon, the state of aggregation appears to have no influence on the amount of adsorption. In examining chemical compounds in which the same element appears, but with differing valencies, it is shown that there is no difference in the quantity of absorption in any case. The relation between the atomic absorption coefficients for most elements has been determined at the medium wave-lengths $\lambda = 0{\cdot}38$, $0{\cdot}36$, $0{\cdot}34$, and $0{\cdot}30 \times 10^{-8}$ cm. Assuming that absorption for hydrogen is exclusively due to scattering produced by the electron combined with the atomic nucleus, it has been found likely that scattering for other elements is solely due to the electrons constituting the outer layer of the respective atoms, that is, to the "outer electrons," and by aid of the relative atomic absorption coefficient for hydrogen, the number of the outer electrons has been estimated for the lighter elements. The atomic absorption coefficient increases for different elements by groups nearly proportionally to the atomic number. If it is accepted that the atomic number gives the number of electrons combined with the atomic nucleus, it is possible from the increase of absorption with increasing atomic number to determine the distribution of electrons between the outer and inner regions. From Barkla and White's determinations of the ratio μ/ρ for copper and water, a formula of the mass scattering coefficient for different elements has been deduced. The values calculated for the relative absorption coefficients for γ-rays agree fairly with the observed absorption coefficients. The value of the mass scattering coefficient of aluminium for γ-radiation, calculated by means of the above-mentioned formula, agrees very nearly with the value directly observed by Ishino. The number of the outer electrons in the lighter elements seems to be the same for the elements placed in the same group of the periodic system, and the distribution of electrons thus appears to be in close connexion with the periodicity of the chemical qualities of the elements as expressed by this system. J. F. S.

Investigation of Röntgen Spectra. *M*-Series. W. Stenström (*Ann. Physik*, 1918, [iv], **57**, 347—375).—The author has investigated the *M*-series of Röntgen spectra for the elements uranium, thorium, bismuth, lead, thallium, gold, platinum, iridium, osmium, tungsten, tantalum, lutecium, ytterbium, erbium, holmium, and dysprosium. It is shown that the older method of measuring Röntgen spectra is not suitable for the soft radiations of the *M*-series, but that better results are obtained if a glowing cathode and high-frequency transformed alternating current are used. As cathode, a Wehnelt cathode was at first employed, but this was later replaced by a tungsten spiral. To find a grating of suitable constant, many crystals were examined and the constant

determined. These included rock salt, $d=2{\cdot}814\times10^{-8}$ cm.; potassium chloride, $d=3{\cdot}136\times10^{-8}$ cm.; calcite, $3{\cdot}028\times10^{-8}$ cm.; gypsum, $7{\cdot}621\times10^{-8}$ cm.; potassium ferrocyanide, $8{\cdot}454\times10^{-8}$ cm.; mica, $10{\cdot}1\times10^{-8}$ cm.; quartz, $4{\cdot}23\times10^{-8}$ cm.; beryl, $4{\cdot}61\times10^{-8}$ cm. (on plane 0.0.0.1) and $8{\cdot}06\times10^{-8}$ cm. (on plane 1.0.1.0); sodium ammonium tartrate, $7{\cdot}30\times10^{-8}$ cm.; sucrose, $10{\cdot}56\times10^{-8}$ cm.; and the compound, $AgNaC_6H_8O_4S_2,Na_2C_6H_8O_4S_2,10H_2O$, $d=19\times10^{-8}$ cm. From a discussion of the sources of error, it is shown that the probable error of the measurements does not exceed 0·2—0·3%. The present measurements were made with a gypsum crystal, and it is shown that, in addition to the α- and β-lines, a γ-line also exists in the M-series, and this conforms to the Moseley relationship. Other lines appear in some cases but these are in all probability due to impurities. Each of the main lines is diffuse and wide, and the blackening decreases with decreasing wave-length. They consist of several single lines, which were not sufficiently separated for characterisation. J. F. S.

Conductivity. IV. Conductivity of Alkaline Earth Formates in Anhydrous Formic Acid. H. I. Schlesinger and R. D. Mullinix (*J. Amer. Chem. Soc.*, 1919, **41**, 72—75. Compare A., 1912, ii, 26; 1914, ii, 703; 1916, ii, 210).—The electrical conductivity of solutions of calcium formate and strontium formate has been determined in anhydrous formic acid solutions at 25°. The conductivity concentration curves are composed of three parts—of two straight lines which intersect at about $N/10$, and a portion which curves upward in a manner similar to that observed for sodium formate (*loc. cit.*). It is likely that these salts ionise into a metal formate ion, which in more dilute solutions is decomposed into a simple metal ion, and that this second ionisation becomes sufficiently great at the concentrations where the two curves meet to affect the conductivity appreciably. J. F. S.

Depolarisers of the Becquerel Effect. Alexander von Samsonow (*Zeitsch. wiss. Photochem.*, 1918, **18**, 141—176).—Working with oxidised copper electrodes, the author has studied the action of certain depolarisers on the electrode when immersed in solutions of sodium sulphate, bromate, iodate, and chlorate. The potential rises much higher in iodate and bromate solutions than in sulphate and chlorate solutions. As depolarisers, ferrous sulphate, glycine developer, sodium sulphite, iron oxalate, *p*-aminophenol, sodium arsenite, and sodium phosphite were used. Working hypotheses of the Becquerel effect and the action of the depolarisers are discussed. J. F. S.

Phenomenon of Electrical Supertension. A. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 375—381. Compare this vol., ii, 8).—A theoretical paper in which an unattackable electrode is considered as a hydrogen electrode from the point of

view of the phase rule. The supertension of electrodes is considered from the same point of view, and a Δ-x diagram is drawn to illustrate the process. It is shown that there is no essential difference between the phenomena of supertension and polarisation. The former is only a little more complicated in so far that here an unattackable electrode has been inserted into the system. When, however, the phenomenon of supertension is considered at attackable electrodes, the process becomes identical with that of polarisation. J. F. S.

Periodic Passivity of Iron. II. A. Smits and C. A. Lobry de Bruyn (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 382—385. Compare A., 1917, ii, 262).—A continuation of previous work in which it was shown that anodically polarised iron could be activated by the introduction of halogen ions. Hence, by the electrolysis of a solution of ferrous sulphate and ferrous chloride, the phenomenon of passivity can be made periodic. This periodic property has now been photographically recorded, together with the time duration of each stage of the process. The potential difference varies between $-0{\cdot}3$ volt and $+1{\cdot}4$ volts with respect to the normal calomel electrode, and the current density changed from 33 milliamperes to 28 milliamperes per sq cm. With a sealed-in electrode 1·5 cm. long, the iron was active for a short period and passive for a comparatively long period. With a smaller current density, the active and passive periods become nearly equal. The effects on the curves produced by changing the relative depth of the electrodes have been studied. Using a larger iron electrode, the potential difference showed irregular oscillations, whilst the current strength was regularly periodic. The irregularity was such that even the most active state did not recur regularly, and the whole curve shows periodicity under the influence of great disturbances. Hence it follows that the electrode was never active throughout the whole area at the same time. This confirms the previous view that the difficulty of rendering iron passive increases with increasing size. J. F. S.

The Sign of the Electrical Phenomenon and the Influence of Lyotropic Series observed in this Phenomenon. H. Zwaardemaker and H. Zeehuisen (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 417—427. Compare A., 1918, ii, 351).—The nebula produced when an unsaturated solution of salicylic acid is sprayed always possesses a negative electric charge. This charge is weakened by both anions and cations, in the order $Li^{\cdot} < Na^{\cdot}, K^{\cdot} < Rb^{\cdot} < Cs^{\cdot} < NH_4^{\cdot}$ for cations, and $CNS', NO_3' < I', Cl', Br', < C_2H_3O_2' <$ tartrate ion $< PO_4''' <$ citrate ion $< SO_4''$ for anions. Acetic acid weakens or completely destroys the negative charge of salicylic acid. In higher concentrations with a positive electrical phase, it prevails as an acid over salicylic acid sprayed in weak solutions, which gives a negative charge. Acetates also have a weakening effect on the charge of salicylic acid, whereas of them-

selves they produce no charge. Mixtures of salicylic and acetic acids showed the electrical property of acetic acid so long as the latter acid is present in the larger quantity. If the concentration of acetic acid in the mixture falls so low that such a solution of acetic acid alone would give scarcely any effect, then the charge of the mixture sinks to zero; in still lower concentrations of acetic acid, the charge reappears, but this time negative. J. F. S.

Dependence of the Magnetic Properties, the Specific Resistance, and the Density of Iron Alloys on their Thermal Treatment. E. GUMLICH (*Zeitsch. Elektrochem.*, 1918, **24**, 372—377).—The density, specific resistance, temperature coefficient of the resistance, the first and second transition points, and the magnetic properties (coercive force, retentiveness, permeability, and hysteresis loss) have been determined before and after annealing processes carried out under various conditions on pure electrolytic iron, commercial iron (seven specimens), iron alloys with carbon (0—1·8%), with silicon (0—8·5%), with aluminium (0—10·5%), and manganese (0—16%). In the case of pure iron, the following values were obtained: D 7·876; specific resistance per sq. mm., 0·0994; temperature coefficient of the resistance between 20° and 100°, 0·51%; saturation value, $4\pi J_{\infty} = 21{,}620$, where J is the intensity of magnetisation. These values were very little changed by annealing and stand in contrast to the magnetic properties. It is shown that the improvement in the magnetic properties brought about by annealing is not due, as generally believed, to a molecular change, but rather to the removal of adsorbed gases. In rich carbon alloys, the first and second transition points lie in the same position as those given in the diagram of condition. In the curves between the carbon content and the density, coercivity and saturation value, respectively, there is a sharp break at the point where, normally, cementite separates from perlite or martensite. The carbon content has a marked effect on the coercive force. This quantity increases approximately 7 gauss per 1% increase in the carbon content in the case of perlite and 70 gauss in the case of martensite. With smaller carbon content, the influence is much greater; thus with 0·1% carbon impurity, the coercive force rises 0·7 gauss. The presence of silicon diminishes the magnetic properties; this substance behaves like non-magnetic impurities, which diminish the magnetic properties of the iron. The presence of aluminium affects the iron in much the same way as silicon; the specific resistance increases nearly proportionally to the aluminium content. The second transition point is lowered 100° by 10% of aluminium. The manganese alloys show similarities to the carbon alloys. The coercive force is extraordinarily high after annealing, and with 10% manganese has a value of 60 gauss, whereas the retentiveness disappears with 14—16% manganese. With manganese concentrations 8—9%, the density, specific resistance, and the magnetic properties show great irregularity. The transition points show a marked tempera-

ture hysteresis, and from this it is deduced that alloys containing 10—12% manganese cannot be magnetised. J. F. S.

Diamagnetism in Weak [Magnetic] Fields. O. E. Frivold (*Ann. Physik*, 1918, [iv], **57**, 471—488).—The magnetic susceptibility of tellurium, water, sulphur, antimony, zinc, gold, and silver has been investigated in magnetic fields of varying strength. With the exception of zinc, all the elements investigated show a dependence, with respect to their susceptibility, on the strength of the field for weak fields. In the case of higher field strengths, the susceptibility is constant except in the case of silver. The susceptibility is constant for field strengths down to 100 gauss in the case of zinc, to 600 gauss for gold, to 250 gauss for antimony, to 200 gauss for tellurium, and above 600 gauss for sulphur. Silver is paramagnetic in weak fields, but becomes diamagnetic in fields above 800 gauss. In the case of antimony, tellurium, and sulphur, a very strong dependence on the field strength for weak fields is displayed. The susceptibility of gold shows a dependence on the field strength which is in keeping with the theory of Gauss, and on the basis of this theory, the number of magnetons per cu. cm. has been calculated and the value $1{\cdot}7 \times 10^{14}$ obtained. Consequently, a magneton of gold contains $3{\cdot}65 \times 10^{9}$ atoms.

J. F. S.

The So-called First Quantum Theory of Planck. The Quantum Theory of Paramagnetism. Adolf Smekal (*Ann. Physik*, 1918, [iv], **57**, 376—400).—A theoretical paper in which three formulæ are deduced to represent susceptibility. These formulæ are tested on measurements for ferric sulphate, manganese sulphate, and the tetrahydrate of manganese sulphate, and a comparison is made with the quanten theories of Planck. J. F. S.

Thermal Conductivity of Neon. S. Weber (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 342—356).—The thermal conductivity of neon has been determined under various pressures by Goldschmidt's method, which consists in electrically heating a wire in the gas and from resistance measurements calculating the rate of conduction. A correction is introduced for loss of heat at the ends of the wire. The thermal conductivity of neon at the following temperatures is shown to be: 105·9°, $k' = 0{\cdot}0001344$; 0°, 0·0001087; −74·37°, 0·0000879; and −181·43°, 0·0000499. These values are compared with the values calculated by means of the formula of Sutherland and a general formula of Maxwell. It is shown that, whilst there is good agreement in the second case, Sutherland's formula appears to be inapplicable at low temperatures. From a comparison of the thermal conductivities of argon, helium, and neon, it appears that the reduced thermal conductivity of neon changes in a different manner with the reduced temperature than the similar values for argon and helium. J. F. S.

Empirical Formula for Calculating the Specific Heat of Water. J. NARBUTT (*Physikal. Zeitsch.*, 1918, **19**, 513—514).—The author has deduced an empirical formula for calculating the specific heat of water over the temperature range 0—100°. This formula is based on the experimental results of Ludin, Dieterici, Bousfield (A., 1911, ii, 580), Callendar (A., 1912, ii, 428), and Barnes and Cooke, and has the form $c_t=1\cdot00733-0\cdot0007416t+0\cdot000016845t^2-0\cdot00000009552t^3$, where $c_{15}=1$. The agreement between the values calculated by this formula and the best experimental values are extremely good. J. F. S.

Calculation of the Ratio of the Principal Specific Heats of Benzene and *cyclo*Hexane by Leduc's Cyclic Method. G. DÉJARDIN (*Compt. rend.*, 1919, **168**, 161—164).—Using Leduc's formula (compare *Ann. Physique*, 1915, [viii], **23**, 577), the author finds that the value of γ, the ratio of the principal specific heats, for benzene at 20° is $\gamma=1\cdot106$ and at 100° $\gamma=1\cdot116$, and for *cyclo*hexane between 20° and 90° is $\gamma=1\cdot077$. Using the formula $\gamma=1+2/(\mu+\lambda)$, where μ is the number of degrees of liberty relative to the kinetic energy of the molecule and λ is the intramolecular potential energy, the author finds for benzene $\gamma=1\cdot111$ and for *cyclo*hexane $\gamma=1\cdot083$ or $1\cdot074$, according as the degrees of liberty are taken as 24 or 27. W. G.

Thermochemical Studies: Simplified Formula for Calculating the Molecular Latent Heat of Evaporation. DANIEL LAGERLÖF (*J. pr. Chem.*, 1918, [ii], **98**, 136—142).—Since all the author's calculated values and also Thomsen's experimental values for the heats of combustion of the hydrocarbons refer to the gaseous state, whilst most of the experimental values obtained by other authors refer to liquid or solid compounds, comparison of these different values requires a knowledge of the molecular latent heat of evaporation. The latter has been determined in but few cases, and can be derived only from Deprez and Trouton's law, $q/T=$constant. For the value of this constant, van't Hoff deduced the mean value 20·55 cal., whilst for non-associated liquids Kurbatov obtained the mean value 20·7 cal., the variation from the mean being at most 3—4%. From the equation

$$w_{\text{vap.}}=q=20\cdot55T$$

(or $20\cdot7T$), the author derives the expressions $q=0\cdot02t+5\cdot6+0\cdot00055t$ and $q=0\cdot02t+5\cdot65+0\cdot0007t$, which refer to kilogram calories; $t=T-273$. In order to arrive at an expression which may be easily remembered, he combines these two equations, with the result: $q=w_{\text{vap.}}=0\cdot02t+5\cdot6+0\cdot0007t$. The third, variable member of the right-hand side may be neglected for values of t numerically less than 15°. The available experimental data show, however, that for uninuclear, aromatic hydrocarbons a fourth negative member must be introduced, the equation then becoming $w_{\text{vap.}}=0\cdot02t+5\cdot6+0\cdot0007t-(t-80°)/300$. It is not known if cor-

rection is needed for multinuclear aromatic hydrocarbons, since no experimental numbers exist.

The values for the different terms of the above equations and the calculated and experimental values of $w_{vap.}$ are given in tabular form for a large number of hydrocarbons of different kinds. The differences between the calculated and experimental values are sometimes marked, but in most cases the agreement between them is extremely good. T. H. P.

Thermochemical Value of the Linkings Uniting the Atoms in Crystals. M. Padoa (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 327—331).—If the union of the atoms in crystalline networks is affected by means of valency (compare this vol., ii, 51), a relationship should exist between the thermochemical data and the values of such linkings. Since the heat of combustion of diamond is 94·32 Cal. per gram-atom, and $CO + O \longrightarrow CO_2 + 68·22$ Cal., and since the thermochemical equivalence of the four valencies of carbon has been demonstrated, the difference $94·32 - 68·22 = 26·10$ Cal. may be taken as the heat of formation of carbon monoxide from an atom of carbon combined in diamond, and the difference $68·22 - 26·10 = 42·12$ as the heat of disintegration of the carbon atom, that is, the heat-equivalent of the energy required to dissolve the linking holding it in the crystal. From the structure of the diamond, it follows that with each carbon atom there correspond four half-valencies or two whole ones, so that each valency has the value $42·12 : 2 = 21·06$ Cal. A similar value is obtained in the case of graphite.

Each free atom of carbon gives, then, on complete combustion, $94·32 + 42·12 = 136·44$ Cal., and four free hydrogen atoms yield similarly four times the heat of combustion of a gram-atom of molecular hydrogen plus twice the heat of dissociation of the hydrogen molecule, that is, $4 \times 34·35 + 2 \times 95 = 327·40$ Cal. Hence the sum $136·44 + 327·40 = 463·84$ Cal., diminished by the observed heat of combustion of methane, namely, 212·70 Cal., gives 251·14 Cal., which constitutes the heat of formation of the methane molecule from its constituent free atoms; consequently, each C–H linking corresponds with $251·14 : 4 = 62·78$ Cal. Similar calculation of the value of the C–C linkings in normal, saturated, open-chain hydrocarbons gives numbers varying from about 16 Cal. for the lower to about 18 Cal. for the higher members of the series.

In the case of benzene, which, according to Thomsen ("Thermochemistry," 1908, 393, 449), behaves thermochemically as if it contained nine simple linkings, and thus corresponds with the centric formula, each of these nine linkings represents a value of 16·6 Cal. With other cyclic hydrocarbons, increase in the number of nuclei is accompanied by increase in the mean number of linkings competing for each carbon atom, this number tending to the limiting value 2; at the same time, the mean value for each C–C linking increases towards the value, 21·0, for graphite. With hydrogenated hydrocarbons, such as *cyclo*hexane, decahydronaphthalene, and *n*-octane,

the C–C values are somewhat higher than with the corresponding non-hydrogenated ones. T. H. P.

The Heat of Dissociation of Diatomic Gases in Relation to the Increase in the Value of $\sqrt{a}$ of the Dissociated Atoms. J. J. van Laar (*Chem. Weekblad*, 1918, **15**, 1124—1137). —The theoretical considerations of this paper are based on the regularities observed by the author which are found to exist when the values of b and $\sqrt{a}$ of the van der Waals's equation of state are brought into relation to the groups of the periodic system (A., 1916, ii, 386—387, 610; 1917, ii, 67). The values of b and $\sqrt{a}$ for a compound are shown to be additive properties of the substance calculable from the values of the corresponding constants of the constituent elements. The value of b for any element is found to be independent of its state of combination, whether the element occurs free or combined in a molecule. On the other hand, $\sqrt{a}$, which is dependent on the mutual attraction of the molecules, is subject to variation according as the atom to which it relates is more or less shielded by other atoms in the molecule. For example, the values of $\sqrt{a}$ for the carbon atom in CH_4, silicon in SiH_4, nitrogen in NH_3, are in each case found to be zero, that is, the central atom exerts no external attraction. In the case of hydrogen, nitrogen, oxygen, and the halogens, all of which dissociate into single atoms in suitable conditions of temperature, it has been found that $\sqrt{a}$ is greatly increased in the monatomic state of the gas. $\sqrt{a}$ thus becomes a measure of the "valency attraction" of the two atoms ($\sqrt{A}$), whilst the value of $\sqrt{a}$ ordinarily to be attributed to the same atom in compounds represents the "residual attraction." For carbon, the ratio of the two values is 32:3·1. Between the two constants $\sqrt{A_K}$ and $\sqrt{a_K}$ at the critical temperature, the following relation is established:

$$\sqrt{A_K} = \sqrt{a_K} \times \sqrt{(1 + \tfrac{4}{27}\theta Q_0/T_K)},$$

where Q_0 is the energy liberated at $T=0$ in the formation of one gram-molecule of gas from the free atoms, T_K is the critical temperature, and θ a constant approximating to unity. The values of $\sqrt{A}$ for various gases (hydrogen, nitrogen, oxygen, the halogens) calculated from this equation are in satisfactory agreement with the values which correspond with the position of these elements in the periodic arrangement. W. S. M.

The Effect of some Simple Electrolytes on the Temperature of Maximum Density of Water. Robert Wright (T., 1919, **115**, 119—126).

Compressibility of Aqueous Solutions, especially of Urethane, and the Polymerisation of Water. Theodore W. Richards and Sven Palitzsch (*J. Amer. Chem. Soc.*, 1919, **41**, 59—69).—The compressibility of water and of aqueous solu-

tions of urethane has been carried out by the method previously described (A., 1912, ii, 896). The concentration was varied from 0—56·01%, and the compressibility determined for pressures between 100—300 megabars. All experiments were conducted at 20°. In addition to these determinations, the solution volume, the surface tension, and the viscosity of urethane solutions were also determined. It is shown that with rising concentration, the compressibility decreases rapidly from $43{\cdot}25 \times 10^{-6}$ (the compressibility of pure water) to $38{\cdot}91 \times 10^{-6}$, the compressibility of a solution of 34 grams of urethane in 100 grams of water. From this point, the compressibility increases, at first slowly and then more rapidly; at the highest measured concentration, 127·35 grams of urethane in 100 grams of water, the compressibility is $40{\cdot}86 \times 10^{-6}$. The surface tension, specific volume, and viscosity showed no such minimum, and it is shown that none is to be expected. The results emphasise the theory of Whiting, which ascribes polymerisation to water. J. F. S.

Determination of the Compressibility of Solids at High Pressures. Leason H. Adams, Erskine D. Williamson, and John Johnston (*J. Amer. Chem. Soc.*, 1919, **41**, 12—42).—The compressibility of quartz, calcite, aluminium, sodium chloride, lead, brass, cadmium, zinc, tin, silver, copper, gold, bismuth, a tin–bismuth alloy, tool steel, and silica glass has been determined for pressures up to 12,000 megabars. The principle of the method employed is to compare the change of volume under pressure of a cylinder of the material with that of a similar cylinder of soft steel, the compressibility of which was considered to be $0{\cdot}60 \times 10^{-6}$ cm.^{2}/megadyne. In carrying out the determination, the solid, surrounded by a liquid such as kerosene, was enclosed in a thick-walled steel bomb fitted with a movable non-leaking piston, and pairs of simultaneous readings were made of (1) the displacement of the piston, that is, the volume change, and (2) the pressure. The piston displacement was measured to 0·01 mm. by means of a dial micrometer. In measuring the pressure, advantage was taken of the change of resistance under pressure of a "therlo" wire, and in order to determine the pressure to within 1 megabar, the resistance was measured with a type of Wheatstone bridge having no movable contacts. The P-Δv graph for gold, copper, brass, silver, aluminium, and calcite, like that of steel, is linear, but the graph for zinc, tin, cadmium, lead, the tin–bismuth alloy, quartz, bismuth, and sodium chloride shows an appreciable curvature, thus indicating for those substances a measurable decrease of compressibility with increasing pressure. A comparison was made of the compressibility of two alloys with that of their components. In the case of a simple mixture, such as the tin–bismuth alloy, the measurements indicate that the compressibility of mixtures the other properties of which, such as specific volume, electrical conductivity, and specific heat, are approximately linear functions of the composition, is related in the same

simple way to the compressibility of the separate components. On the other hand, the compressibility of alloys of the class to which brass belongs is much lower than the sum of the individual compressibilities. J. F. S.

Thermal Dissociation of Sulphur Dioxide. J. B. Ferguson (*J. Amer. Chem. Soc.*, 1919, **41**, 69—72. Compare this vol., ii, 15).—Starting from the equilibrium constant of the reaction $CO+\frac{1}{2}SO_2 \rightleftharpoons CO_2+\frac{1}{4}S_2$, the author has calculated the degree of dissociation and the equilibrium constants of sulphur dioxide over the temperature range 1000—1500° and at pressures from 1 atm. to 0·001 atm. The degree of dissociation at 1500° and 1 atm. is found to be 5·9, whilst at 0·001 atm. it is 59. Consequently, it is obvious that the dissociation of sulphur dioxide is less than the dissociation of either carbon dioxide or water vapour. J. F. S.

Capillarity Constants of Pure Mercury and of Liquid Potassium Amalgam in Contact with Potassium Iodide Solutions. V. Polara (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 322—327).—Gouy (A., 1892, 760) showed that the capillarity constant of mercury in contact with aqueous potassium iodide solutions assumes a maximum value somewhat less than that of the same metal in contact with dilute sulphuric acid (1 : 6 by vol.). This behaviour is in contradiction to Lippmann's law, according to which the capillarity constant should be a function solely of the potential difference at the contact, and its maximum hence independent of the nature of the substances in contact. By means of Quincke's apparatus, the author has investigated the influence of the concentration of the potassium iodide on the maximum value of the capillarity constant of the mercury in contact with it and on the polarisation determining such maximum. Gradual increase of the concentration is found to be accompanied by progressive lowering in the maximum value of the capillarity constant, the difference for the two extreme cases ($N/10$ and $10N$) amounting to a variation of about 1 mm. in the difference of level between the two limbs of the apparatus; within the limits of sensitiveness of the method, the polarisation requisite for obtaining the maximum depression does not appear to be influenced by the concentration. Depression of the surface tension of the solution by addition of ethyl alcohol in various proportions produces marked lowering of the maximum of the capillarity constant, especially for percentages of the alcohol not exceeding 40; for higher proportions of alcohol, the effect is less pronounced. Also, potassium amalgams (2—0·1 part of potassium per 1000 of mercury) in contact with normal potassium iodide solution exhibit a capillarity constant which is somewhat lower than the maximum capillarity constant of pure mercury in contact with sulphuric acid solution, and diminishes sensibly with increase of the proportion of potassium dissolved in the mercury, the diminution being slower for the more concentrated than for the more dilute amalgams.

Study of the variations in the density of the electric double layer at the contact with the polarisation by an apparatus detecting a change of 0·1 volt in the polarisation confirms the relation $X = -dA/dp$, where X is the density of the double layer, A the capillarity constant, and p the polarisation. This relation may be brought into accord with the circumstance that the capillarity constant does not depend solely on the potential difference at the contact by assuming that the function A has the form $A = S - T(V - p)$, where S, the ordinary surface tension, is independent of the potential difference at the contact, but depends, in agreement with the results obtained, on the particular conditions of the contact; $T(V - p)$ is the symbol of a function only of the potential difference $(V - p)$ existing at the contact for each value of the polarisation employed (V = potential difference due to the contact and p the polarisation employed), and satisfying also the conditions $dT/dp = X$ and $(dT/dp)_{p=V} = 0$. T. H. P.

Velocity of Diffusion. Philipp Frank (*Physikal. Zeitsch.*, 1918, **19**, 516—520).—A mathematical paper in which formulæ are deduced for the velocity of diffusion of gaseous molecules. The calculations are based on considerations of the Brownian movement, and are made in connexion with single particles and with the rate of advance of the "head" of a particle swarm.

J. F. S.

Crystal Assemblage in Relation to the Atomic Field of the Crystal. R. Gross (*Jahrb. Radioaktiv. Elektronik.*, 1918, **15**, 270—292).—The author uses the term "Sammelkrystallisation" (crystal assemblage) to signify the transformation of a substance from an amorphous or sub-crystalline to a distinctly crystalline state. A number of examples of the phenomenon are discussed. One of the most striking examples is a process used for making tungsten filaments. The finely divided metal, obtained by reduction of the oxide, is pressed into the form of wire and drawn slowly through a small heated coil at a temperature of 2000—2200°. When the rate of passage of the wire through the heated coil is properly regulated, it becomes converted into a single homogeneous, elongated crystal, the rate of growth of the crystal being equal to the rate at which the wire is travelling. The particles of tungsten of which the wire is originally composed have a mean diameter of about 10^{-5} cm., and it has been shown by Debye (A., 1917, ii, 574) by the X-ray method that this powder consists of cubic, crystalline particles. Other examples of crystal assemblage are afforded by the increase in size of the crystals of many metals by annealing, by the formation of silver crystals from a silver sol, and by the formation of calcite crystals when powdered calcium carbonate is heated under pressure. Some substances, for example, calcium sulphate, have a greater solubility than the normal when the particles in equilibrium with the solution are very small in size, but in course of time the solu-

bility falls to the normal owing to increase in the size of the particles. It is shown thermodynamically that the solubility should increase when the particles become very small, and it is concluded that the theory of minimum surface energy does not adequately explain crystal growth, since for very small particles the surface energy is not independent of the size. E. H. R.

Liquid Crystals. II. Melting and Congelation Phenomena with *p*-Azoxyanisole. W. J. H. Moll and L. S. Ornstein (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 254—258).—In a previous paper on the extinction of liquid crystals, it was suggested that two varieties of liquid crystals of *p*-azoxyanisole exist, ex-solid (produced by melting the solid) and ex-liquid (produced by cooling the isotropic liquid). To confirm this point, the authors have determined the fusion and congelation curves of *p*-azoxyanisole, and show from the results that there is no evidence from this source of the existence of two forms of liquid crystals of *p*-azoxyanisole. On the other hand, these curves show the existence of three solid forms of this substance: *p*-azoxyanisole I (m. p. 118°), *p*-azoxyanisole II (m. p. 104·5°), and *p*-azoxyanisole III (m. p. 116°). A fourth form, which melts at 108°, was shown to exist in the previous paper, but this form did not appear in the present work, and it is now shown only to be capable of existence in capillary layers (between glass). J. F. S.

Molecular Mechanism of Colloidal Behaviour. I. The Swelling of Fibrin in Acids. Richard C. Tolman and Allen E. Stearn (*J. Amer. Chem. Soc.*, 1918, **40**, 264—272).—The amount of swelling of blood fibrin in solutions of hydrochloric, nitric, sulphuric, acetic, and formic acids of various concentrations has been determined, as well as the amount of acid adsorbed by the fibrin from the solution. Similar experiments have been carried out with solutions of sodium chloride and with solutions of the above-named acids to which sodium chloride has been added. The data obtained are in accordance with the authors' theory of the molecular mechanism of protein swelling. This theory embraces the following points. On account of the amphoteric nature of protein colloids, they possess a marked tendency to adsorb hydrogen ions from acid solutions and hydroxyl ions from alkaline solutions. In an acid solution, the adsorbed hydrogen ions, together with an equivalent number of anions, form a "double layer" on the walls of the pockets or pores in the interior of the gel, and this leads to swelling and the imbibition of water by electrostatic repulsion. The addition of a strong electrolyte to such a swollen colloid, either a neutral salt or excess of the strong acid which caused the original swelling, will furnish ions in the interior of the pockets which will tend to arrange themselves so as to neutralise the electrical fields of the adsorbed layers, and thus bring about a reduction of the swelling. The addition of a neutral salt to an acid solution tends to neutralise the electrical field of

the adsorbed acid, and hence makes it easier for more acid to reach the surface of the pockets, thus leading to increased adsorption. Salts with multivalent ions should be more effective in reducing swelling than salts with univalent ions, since, for example, a bivalent ion will take up no more room than a univalent ion and will be twice as effective in neutralising an existing electric field. No assumptions are made as to the molecular nature of the adsorption of the hydrogen or hydroxyl ions; the theory would be equally tenable if the adsorption process should lead to a fairly uniform coating of ions over the whole of the exposed surface, or, on the other hand, if the hydrogen ion should only tend to go on to the protein molecule at special points where there is a particularly strong stray field, for example, where the amino- and acid groups of the amino-acids approach one another. J. F. S.

Colours of Colloids. WILDER D. BANCROFT (*J. physical Chem.*, 1918, **22**, 601—630).—A theoretical paper in which the author discusses the nature of the colour of natural objects. The subject is treated historically, and the various types of colouring individually treated. Colours are divided into two groups: (1) structural colours, and (2) pigmentary colours. The former group of colours owes its existence to the refraction, absorption, and interference of light. J. F. S.

Degree of Dispersion of Colloids and its Determination. GEORGE KING (*J. Soc. Chem. Ind.*, 1919, **38**, 4—7T).—A short account is given of the slit ultra-microscope and its capabilities. In counting the number of colloidal particles in a definite volume of colloidal solution, it is necessary, owing to the rapid Brownian movement, to take the mean of the numbers of particles observed at ten momentary observations, and the solutions should be diluted with colloid-free medium until there are never more than four particles in the field at the same time. The periodic illumination may be effected by allowing a pendulum screen to swing in front of the micrometer slit, the impression of the number of particles seen being then very definite. The solution in the observation cell should be changed at least ten times, and the mean of the one hundred separate counts taken; further, one or more controls with fresh dilution should always be made.

The paraboloid, Leitz, and Cotton and Mouton devices for dark-ground illuminations serve well for qualitative observation, but are useful only for coarse hydrosols; they are, moreover, unsuitable for the rapid examination of colloidal solutions, as the adjustment of the instrument must be disturbed for each small quantity observed and a fresh volume of solution introduced into the special microscope slide. With the cardioid ultra-microscope, it is possible to distinguish particles beyond the range of the old slit ultra-microscope, owing to the fact that the hydrosol can be more intensely illuminated. The slit ultra-microscope has now been enhanced in sensitiveness by using objectives of high numerical

aperture (1·05), one at right angles to the other, the front lenses, made of quartz, being both immersed in the hydrosol. By this means, the size of the particles which can be counted is diminished from 5 $\mu\mu$ to 3 $\mu\mu$, whilst even smaller particles can be seen in concentrated solution, but not accurately counted in dilute solution.

With the new immersion ultra-microscope, qualitative examinations were made of solutions of peptone, starch, gelatin, agar-agar, and dextrin in the concentrations used by Findlay and King (T., 1913, 1170; 1914, 1297), but these were found to be optically clear under the best conditions for illumination, etc.; the refractive indices of the medium and colloid are doubtless nearly equal. Merck's ferric hydroxide is, however, countable.

Of physiological interest is the condition of casein in cow's milk and human milk. The particles in the latter are uncountable in the slit ultra-microscope, but they can be counted in the new instrument, whilst casein in cow's milk is easily seen in the slit ultra-microscope. Thus it would seem that, when it is to be used for feeding infants, cow's milk should be so treated as to cause an increase in the degree of dispersion of the casein particles; this is not effected by mere dilution of the milk.

When it is necessary to determine the size of microscopic particles in a suspension, use may be made of Stokes's formula, $V=F/6\pi\eta r$, where V=velocity of fall, F=force acting, η=viscosity, and r=radius of particle. Other methods which have been used are discussed by Henri (*Trans. Faraday Soc.*, 1918, 47), but are not convenient for technical application. T. H. P.

The System Iron–Oxygen. A. Smits and J. M. Bijvoet (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 386—400).—A theoretical paper in which the three-phase systems FeO,Fe,gas and Fe_3O_4,FeO,gas are considered. The gas in question is either of the reducing mixtures CO_2,CO, or H_2O,H. On the basis of the deductions drawn from the above-mentioned considerations, the processes operative in the blast furnace are theoretically investigated. The *P.T.* diagram of the system oxygen–iron is derived from the equilibria of the iron oxides in reducing and oxidising gases respectively. Calculations are made of the oxygen dissociation tension, and these values, as was to be expected, are very small. J. F. S.

Influence of Temperature on Homogeneous Gas Reactions. George W. Todd and S. P. Owen (*Phil. Mag.*, 1919, [vi], **37**, 224—230).—A mathematical paper in which from Maxwell's distribution theorem an expression has been deduced by which the number of molecules having a velocity greater than a particular value may be calculated. This expression has the form

$$n=2Ne^{-x^2}/\sqrt{\pi}(x_1+\tfrac{1}{2}x_1),$$

in which n is the number of molecules per c.c. which have a velocity greater than c, and $x=c\sqrt{m/2R\theta}$; all the other factors have their usual significance. Assuming that only molecules with kinetic

energies greater than a definite minimum have the power to react with other molecules, it is shown how the velocity constant of a gaseous reaction varies with temperature. This is represented for the general case by the equation

$$k_{\theta_2}/k_{\theta_1} = \phi\theta_2/\phi\theta_1(e^{W(1/\theta_1 - 1/\theta_2)}),$$

in which W is a constant. The general relationship for the dependence of the equilibrium constant on the temperature is also deduced. J. F. S.

The Evolution and Magnetic Properties of Chromic Hydroxide in Alkaline Solution. F. Bourion and A. Sénéchal (*Compt. rend.*, 1919, **168**, 89—91. Compare this vol., ii, 66).—The velocity constants for the rate of oxidation of chromic hydroxide in alkaline solution by hydrogen peroxide at 17° and 30° during the first eight hours correspond fairly well with those for a quadrimolecular reaction. The paramagnetism of an alkaline solution of chromic hydroxide diminishes slowly with time, but the diminution is small and never exceeds 20%. W. G.

Polar and Non-polar Valency. Rajendralal De (T., 1919, **115**, 127—134).

Automatic Variation of Gas Pressure and its Application to a Vacuum Pump, Circulation of Gases [and] Magnetic Stirrer. O. Maass (*J. Amer. Chem. Soc.*, 1919, **41**, 53—59).—An apparatus is described which, when attached to a Toepler mercury pump, may be used for the periodic variation of gas pressure. By suitable adjustments, which are described in the paper, the apparatus may be employed for the circulation of gases and for working a magnetic stirrer. J. F. S.

Inorganic Chemistry.

Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. I. W. E. Adeney and H. G. Becker (*Sci. Proc. Roy. Dubl. Soc.*, 1918, **15**, 385—404).—The rate of solution of nitrogen and oxygen in distilled water, tap-water, and sea-water has been determined at temperatures between 11·3° and 12·3° by allowing a bubble of the air to pass up a narrow glass tube containing the water. This affects the mixing of the solution and constantly exposes the air to a fresh surface of water. The object of the experiments was to substantiate the authors' views on the mechanism of solution of a gas in the liquid. Contrary to the generally accepted view, it is held that the gas is

absorbed by the surface layer, but the gases do not remain concentrated here; they are gravitationally drawn downwards through the lower layers of water with comparative rapidity (compare *ibid.*, 1914). J. F. S.

Flame Reactions: Selenium and Tellurium in the Hydrogen–Air Flame. Jacob Papish (*J. physical Chem.*, 1918, **22**, 640—646).—The elements selenium and tellurium, as well as their dioxides and hydrides, have been introduced into the hydrogen air flame and the colour changes observed. At the same time, experiments were made to ascertain the nature of the deposit, if any, on a cold object introduced into the flame. Selenium dioxide produces a deep blue luminescence in the inner zone, pale blue in the middle zone, and green in the outer zone. There was a deposition of selenium in the inner and middle zones, but no deposition in the outer zone. Hydrogen selenide produces a very faint blue luminescence in the inner zone, deep blue in the middle zone, and green in the outer zone. There was a deposition of selenium in the inner zone, but no deposition elsewhere. Selenium produces a luminescence coloured blue, violet, and green in the inner, middle, and outer zones respectively; in this case and in all following cases, the element was deposited in the inner and middle zones, but there was no deposition in the outer zone. Tellurium dioxide, hydrogen telluride, and tellurium all produce a lilac luminescence in the middle zone and a green luminescence in the outer zone, whilst tellurium dioxide and the free element produce a green luminescence in the inner zone, whereas the hydrogen telluride produces a blue luminescence in this region. Possible explanations for the differences in the various cases are suggested. J. F. S.

The Constitution of Nitrous Vapours. P. Jolibois and A. Sanfourche (*Compt. rend.*, 1919, **168**, 235—237).—When nitric oxide and oxygen are mixed at the ordinary temperature in the proportion of 4:1 by volume, combination is instantaneous, and nitrogen trioxide is formed and remains unchanged. If the gases are mixed in the proportion of 2:1, or if an excess of oxygen is used, the combination rapidly reaches the stage of the trioxide, but after twenty seconds 34% of the peroxide is formed, after thirty-seven seconds 68%, and after 100 seconds 92%. If nitrous vapours are heated at 400°, the equilibrium tends towards the formation of the trioxide, with partial destruction of the nitrous vapours. W. G.

The Synthesis of Ammonia at High Temperatures. III. Edward Bradford Maxted (T., 1919, **115**, 113—119).

Production of Ammonia from "Nitrolime," and the Time Yield under Various Conditions. Werner Grahmann (*Zeitsch. Elektrochem.*, 1918, **24**, 385—391).—The rate of produc

tion of ammonia from boiling mixtures of "nitrolime" and water, "nitrolime" and sodium hydroxide or sodium carbonate of various concentrations, and "nitrolime" and potassium hydroxide or carbonate of various concentrations has been determined. In the case of "nitrolime" and water, it is shown that the rate of decomposition of calcium cyanamide is extremely slow in all concentrations at the boiling point and atmospheric pressure. Thus a 1% solution is decomposed to the extent of 98% by seventy-two hours' boiling. In the presence of sodium carbonate, the decomposition really amounts to the decomposition of sodium cyanamide (*a*) under a constant sodium hydroxide concentration, and (*b*) under a concentration of sodium hydroxide, which increases during the reaction. In the case of an addition of sodium hydroxide, the decomposition takes place under a regularly increasing concentration of the hydroxide. The same remarks apply to the decompositions in the presence of potassium carbonate and hydroxide. The presence of alkali hydroxide or alkali carbonate has an accelerating influence on the reaction; the velocity increases with increasing concentration of the added salt to a maximum, after which it remains more or less constant. The maximum in the case of alkali hydroxides occurs with much lower initial concentration of alkali than in the case of the alkali carbonates, for in these experiments the alkali concentration increases continuously from beginning to end of the decomposition. The experiments with potassium hydroxide and carbonate do not show the same maximum as the sodium compounds under similar conditions, so that, since sodium hydroxide and potassium hydroxide are ionised to practically the same extent, it must be taken that the acceleration of the decomposition velocity is not dependent entirely on the hydroxyl-ion concentration, but that the cation and the undissociated molecules also exert a specific action. A number of orientating experiments were carried out under 30 atmospheres pressure at 150°. Under these conditions, it is shown that, even without the addition of alkali, the decomposition takes place very rapidly until 75% of the calcium cyanamide is decomposed, after which the velocity becomes much less, thus: in an aqueous solution 75% is decomposed in forty-five minutes, but only 90% is decomposed in 120 minutes. In the presence of 10% alkali hydroxide, 75% decomposition is reached in thirty minutes and 90% in seventy-five minutes. The "nitrolime" used in the experiments contained 16·85% of cyanamide nitrogen, 0·65% of dicyanodiamide nitrogen, 22·30% free lime, and 0·31% sulphur.

J. F. S.

Effect of Phosphine and Hydrogen Sulphide on the Oxidation of Ammonia to Nitric Acid. Guy B. Taylor and Julian H. Capps (*J. Ind. Eng. Chem.*, 1919, **11**, 27—28).—Pure acetylene has no effect on the catalytic oxidation of ammonia to nitric acid in presence of platinum (compare A., 1918, ii, 265), the opposite results obtained earlier being due to the fact that the acetylene used contained small proportions of phosphine.

Hydrogen sulphide in low concentrations has no immediate toxic effect on the catalytic oxidation. [See *J. Soc. Chem. Ind.*, March.] T. H. P.

Oxidation of Coal. J. R. Partington (*Chem. News*, 1919, **118**, 50—51).—The experimental results obtained by Wheeler (T., 1918, **113**, 945) are discussed, and an alternative explanation offered. The assumption that air is absorbed by freshly won coal with formation of an additive compound, such as a complex oxide, is an improbable one. The facts agree better with the hypothesis that the process is one of adsorption, followed by direct formation of carbon monoxide. Carbon dioxide may be produced by oxidation of the carbon monoxide by moisture, or even by interaction of carbon and water, hydrogen being formed at the same time. The adsorption hypothesis explains the differences observed when moist or dry air is used. In absence of moisture, the proportion of carbon dioxide formed would be expected to be lower than when moisture is present. The fall of the ratio CO_2/CO with rise of temperature also follows from the adsorption hypothesis. E. H. R.

The Interaction of Stannous and Arsenious Chlorides. Reginald Graham Durrant (T., 1919, **115**, 134—143).

Stable Solution of Silver Nitrate. F. Liebert (*Chem. Weekblad*, 1919, **16**, 74).—The solution of the salt is exposed to the light until the organic matter present is exhausted, and is then filtered through asbestos. The resulting solution may be kept in light without further alteration. W. S. M.

Atomic Weight of Lead from Samarskite. Arthur L. Davis (*J. Physical Chem.*, 1918, **22**, 631—639).—Using a specimen of lead obtained from samarskite which contained U_3O_8 12·21% and ThO_2 1·03%, the author has determined the atomic weight of this element. The method adopted was that of Baxter and Grover (A., 1915, ii, 456), and consisted in converting lead chloride into silver chloride. In three experiments, results varying from 206·246 to 206·363 were obtained for the atomic weight of lead. Calculations made from the content of samarskite on thorium and uranium lead to a value of 206·06 for the lead contained in this mineral, whereas the experimental value is 206·30. This corresponds with a mixture of 3 parts of radio-lead and 1 part of ordinary lead. If it is assumed that 8% of the uranium is transformed along the actinium series to form a stable isotope of atomic weight 210, the value 206·38 is calculated for the atomic weight of samarskite lead. The experimental value, however, is in better agreement with the supposition that either or both of the isotopes of lead in the thorium series are relatively short-lived, and that the lead in samarskite represents a mixture of radio-lead of the uranium series, atomic weight 206, and radio-lead of the actinium

series, atomic weight 210. This conclusion is not in agreement with the value 206·04 found by Hönigschmidt for the atomic weight of lead from crystallised uraninite (A., 1914, ii, 653).

J. F. S.

The Sub-acetate and Sub-sulphate of Lead. Henry George Denham (T., 1919, **115**, 109—113).

The Rusting of Iron on Contact with other Metals and Alloys. O. Bauer and O. Vogel (*Mitt. k. Materialsprüf*, 1918, **36**, 114—208).—A discussion of previous work and new experiments on the influence of other metals on the corrosion of iron in conductivity water, distilled water, and chiefly 1% sodium chloride solution. Much attention is paid to the potential difference between the metals and electrolyte, which was measured as follows: the cell, together with a millivoltmeter and a resistance of 100,000 ohms, is placed in parallel with a standard resistance, W. A small current, i, is passed, which is adjusted until no deflection of the galvanometer is obtained, when the potential difference $= iW$. A large number of results are given for the potential difference of pure metals and graphite against the normal calomel electrode. The contact of two metals in the 1% salt solution results in a large increase in the corrosion of the more electro-negative metal, that of the more electro-positive one being reduced. In the water this effect is much less marked. Rusting of iron is entirely prevented when a current was passed which counterbalanced the solution pressure in the electrolyte, so rendering the passage of the ions into solution impossible. For electrolytic iron in 1% sodium chloride solution at 18°, a minimum current density of 0·0000106 amps. per sq. cm. is required, calculated from the formula $(a \,.\, F)/(\mathrm{Fe}/2 \,.\, qs)$, where a is the loss of weight of the iron in grams, F 96,540 coulombs, Fe/2 half the atomic weight of iron, q surface of iron in sq. cm. exposed to attack, and s duration of corrosion in seconds. [See, further, *J. Soc. Chem. Ind.*, March.]

F. C. Th.

Investigation of the Crystal Structure of White and Grey Tin by means of *X*-Rays. A. J. Bijl and N. H. Kolkmeijer (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 405—408).—The structure of the two allotropic modifications of tin has been investigated by means of *X*-rays. The method adopted was that due to Debye and Scherrer, and the interference photographs obtained indicate that both forms of the metal are crystalline.

J. F. S.

Reduction of Osmium Tetroxide by Hydrogen Chloride. Otto Ruff and Susanne Mugdan (*J. pr. Chem.*, 1918, [ii], **98**, 143—144).—The conclusion drawn by Milbauer (A., 1918, ii, 202) that osmium tetroxide is reduced to osmium monoxide by hydrochloric acid is opposed to the results obtained by Ruff and Bornemann (A., 1910, ii, 305) and by Ruff and Rathsburg (A., 1917,

ii, 323), and repetition of Milbauer's experiments by the authors shows that the tetroxide undergoes reduction to a slight extent to the dioxide, but not to the monoxide; the bulk of the tetroxide remains unchanged in the hydrochloric acid solution. Milbauer's erroneous results appear to be due to the presence in the tetroxide of impurities, although the commonest of these, namely, ruthenium tetroxide, behaves similarly to osmium tetroxide. T. H. P.

Mineralogical Chemistry.

Fibrous Quartz from Rhode Island. Alfred C. Hawkins (*Amer. Min.*, 1918, **3**, 149—151).—Fibrous quartz resembling asbestos in appearance, and consisting of long, delicate, flexible fibres, fills narrow veins in metamorphic slates at several localities in Rhode Island. It ranges in colour from pure white to green. The green colour is due to the presence of admixed actinolite, as shown by microscopical examination and by the following analyses: I, green from Fenner's Ledge, Cranston; II, white from the same locality; III, green from Portsmouth.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	CO_2.	S.	Total.
I.	77·15	8·72	7·68	0·70	3·96	1·40	—	0·52	100·13
II.	94·92	4·56		trace	trace	0·16	—	—	99·64
III.	91·83	1·61	3·81	0·80	1·37	0·70	0·50	0·12	100·74

L. J. S.

Hambergite from Kashmir. R. C. Burton (*Rec. Geol. Survey India*, 1913, **43**, 168—172).—Crystals of hambergite, together with cookeite, prehnite, tourmaline, beryl, euclase (?), and amblygonite, have been found in the granitic débris in the Kashmir sapphire mines. They were probably derived from the neighbouring pegmatites. A description is given of a twinned crystal. Analysis gave:

GlO.	B_2O_3.	H_2O.	Total.	Sp. gr.
52·40	[37·39]	10·21	100·00	2·36

L. J. S.

Phosphorite from the Island of Juan de Nova, Madagascar. J. Orcel (*Bull. Soc. franç. Min.*, 1918, **41**, 104—108).—The phosphate deposits on the small island of Juan de Nova, or St. Christophe, about eighty miles off the west coast of Madagascar, have been formed by the action of soluble phosphates, derived from guano, on the underlying coral-rock. Analysis I is of brown, concretionary phosphorite, and II of brown, earthy material of prac-

tically the same composition. The latter is worked under the name "leached guano." The analysis (I) shows an excess of 8·45% CaO, indicating the voelckerite formula $3Ca_3(PO_4)_2,CaO$ (A., 1912, ii, 565).

	CaO.	SrO.	MgO.	Al_2O_3.	P_2O_5.	Cl.	SO_3.
I.	48·63	0·17	1·75	0·15	35·56	0·29	0·56
II.	46·85		n.d.	0·38	35·19	0·14	0·58

	CO_2.	Organic matter.	H_2O.	Loss at 110°.	Insol.	Total.
I.	0·14	1·27	7·97	4·00	0·05	100·54
II.		10·08		5·32	0·03	98·57

L. J. S.

The Colour Change in Vivianite. THOMAS L. WATSON (*Amer. Min.*, 1918, **3**, 159—161).—The large, pale green crystals of vivianite from Plant City, Florida (A., 1918, ii, 119), are non-pleochroic and yield a colourless powder. This powder rapidly changes, especially in sunlight, to deep blue, and becomes strongly pleochroic. An unground sample of the crystals showed FeO 42·88%, whilst the finely ground material gave FeO 38·43%. The change in colour and pleochroism is thus due to the partial oxidation of the iron, and not to inversion as was at first suggested by the microscopical aspect of the material. A tabulation of the refractive indices of pale green and of dark blue vivianite from various localities indicates that the oxidation has been accompanied by an increase in the values of β and γ. L. J. S.

Copiapite in Coal. WILLIAM J. MCCAUGHEY (*Amer. Min.*, 1918, **3**, 162—163).—A specimen of pale green, fibrous melanterite from the Congo coal mine in Perry County, Ohio, changed in the course of a year to dull white, and the fibres became brittle. Yellow spots also developed, especially at the points of contact between the melanterite and the associated shale. This yellow material consists of minute, tabular crystals, and is proved by the following analysis and refractive indices to be copiapite, $Fe_2O_3,5SO_3,18H_2O$.

SO_3.	Fe_2O_3.	H_2O.	Insol.	Total.	α.	β.	γ.
39·68	29·98	30·45	0·31	100·42	1·525	1·545	1·595

L. J. S.

Nasonite from Långban, Sweden. G. AMINOFF (*Geol. För. Förh.*, 1916, **38**, 473).—This mineral, hitherto known only from Franklin, New Jersey (A., 1900, ii, 89), has been observed at Långban in the veins of "secondary calcite," where it is associated with schefferite, native lead, apophyllite, etc. It forms white to pearl-grey lamellar masses, or, less often, hexagonal prisms with

rounded faces. Refractive indices (Na), $\omega = 1{\cdot}9453$, $\epsilon = 1{\cdot}9710$. Analysis by R. MAUZELIUS agrees with the usual formula $Pb_4(PbCl)_2Ca_4(Si_2O_7)_3$.

SiO_2.	PbO.	FeO.	MnO.	CaO.	MgO.	Cl.	H_2O.	Total.
18·23	67·67	0·04	0·14	11·29	0·20	2·90	0·24	100·71

L. J. S.

Anorthite from Japan. S. KÔZU (*Sci. Rep. Tôhoku Imp. Univ.*, 1914, Geol. Ser., **2**, 7—33).—The results are given of elaborate determinations of the optical constants (refractive indices, optic axial angle, and dispersion of the optic axes) for different wave-lengths of anorthite from three Japanese localities. As these show certain differences amongst themselves, the following analyses, by H. S. WASHINGTON, were made of I, anorthite crystals from Miyake-jima, one of the Seven Izu Islands south of Tokyo, and II, crystals from the Tarumae volcano in Hokkaidô.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	Total.	Sp. gr.
I.	44·49	36·00	0·08	19·49	0·04	0·03	0·59	100·72	2·758
II.	44·03	35·93	0·10	18·66	trace	0·07	1·00	100·24	2·757

Barium and strontium are absent, and the slight differences in composition cannot be correlated with the differences in the optical constants. I corresponds with $Ab_{3\cdot9}An_{95\cdot4}Cg_{0\cdot7}$ and II with $Ab_{4\cdot7}An_{92\cdot6}Cg_{2\cdot0}Or_{0\cdot6}$. The melting points are 1538° and 1536° ± 2° respectively. L. J. S.

Racewinite, a New Mineral from Utah. A. N. WINCHELL (*Econ. Geol.*, 1918, **13**, 611—615).—The mineral occurs as veins and irregular masses in limestone, and also replacing the carbonate portion of calcareous sandstones, near the contact with porphyry in the Highland Boy mine at Bingham, Utah, where it is often intergrown with pyrites and other ore minerals. It is brownish-black with a dull to bright lustre, and somewhat resembles coal in appearance. When freshly taken from the mine, it is bluish-green; the change in colour to brownish-black takes place slowly throughout the whole mass, and after six months the largest pieces were altered to the centre. The mineral undergoes other remarkable changes in colour. In boiling nitric acid it is insoluble, but gradually changes to yellowish-brown and translucent. In hydrochloric acid, it is slowly soluble and shows the same change in colour. Thin splinters and particles under the microscope are pale to brownish-yellow. In clove-oil this colour changes first to grass-green and then to black, but the same change does not take place in cedar-oil and some other oils. The finely powdered mineral is nearly white with a yellow tinge. The material is coarsely crystalline with no cleavage or crystal-faces; it is friable and the fracture conchoidal. Sp. gr. 1·94—1·98, H 2½; optically biaxial with large angle and negative, n about 1·51. It adheres to the tongue and slakes in water, breaking up with a sharp, audible

sound. Analyses I and II by J. P. Hickey and C. L. Austin respectively:

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O.	Total.
I.	43·92	23·68	7·37	2·52	0·50	22·04	100·03
II.	43·24	23·69	8·05	2·42	0·78	21·80	99·98

A sample of the green, unaltered mineral showed 0·60% FeO. Over sulphuric acid, 7—8% H_2O is lost in one day and 14% after forty-nine days; this is re-absorbed from a moist atmosphere. Other determinations gave the loss at 70° as 8% and at 200° as 12·1%. Heated to dull redness, the crystal structure is not destroyed, and the optical characters are not materially altered.

L. J. S.

New Swedish Minerals. Gust. Flink (*Geol. För. Förh.*, 1917, **39**, 426—452).—*Ektropite* forms crusts of small, brown, rectangular plates on garnet with calcite and barytes in magnetite ore from the Norrbotten mine at Långban. The crystals are monoclinic ($a:b:c=0·74:1:0·84$, $\beta=61°5'$) with a tabular habit parallel to the orthopinacoid and elongated in the direction of the axis of symmetry. They are opaque with a vitreous to silky lustre, but in thin splinters under the microscope, the material is translucent and yellow. D 2·46, H 4, n 1·62—1·63. Analysis I, by N. Sahlbom, gives the formula $12RO,8SiO_2,7H_2O$. The mineral is related to caryopilite and neotocite.

	SiO_2.	Sb_2O_5.	PbO.	Al_2O_3.	Fe_2O_3.	FeO.
I.	35·02	—	—	0·75	—	5·80
II.	7·75	20·76	—	9·50	3·58	2·44
III.	34·72	—	41·74	—	—	—

	MnO.	CaO.	MgO.	H_2O.	Total.
I.	37·20	3·59	7·20	8·89	99·89*
II.	52·61	0·58	3·06	0·11	100·39
III	2·17	20·28	0·20	0·10	99·90†

* Including K_2O 1·13, Na_2O 0·12, metallic sulphides 0·19.
† Including BaO 0·69.

Katoptrite occurs as tabular crystals and irregular lumps with magnetite in granular limestone in the Brattfors mine at Nordmark. The crystals are monoclinic ($a:b:c=0·79223:1:0·48985$, $\beta=78°57'$) and have a highly perfect cleavage parallel to the orthopinacoid $a(100)$. This cleavage resembles that of mica, but the cleavage flakes are very brittle and not flexible. D 4·5, H $5\frac{1}{2}$. The mineral is black and opaque with a bright metallic lustre. Thin flakes are red by transmitted light and strongly pleochroic. Analysis II, by R. Mauzelius, gives the ratios

$$14RO,2(Al,Fe)_2O_3,Sb_2O_5,2SiO_2.$$

The mineral resembles manganostibite in appearance, and it may perhaps be identical with the incompletely described hematostibite.

Margarosanite (A., 1916, ii, 532).—This new mineral has been found in some quantity in the "Lukas Ort" and Bjelkes shaft at Långban, where it is associated with nasonite, schefferite, apo-

phyllite, calcite, etc. The masses, weighing up to 1 kilo., are snow-white with pearly lustre and columnar structure. Crystals are rare; these are triclinic ($a:b:c=0{\cdot}74998:1:1{\cdot}2849$, $\alpha=74°37'$, $\beta=50°28'$, $\gamma=78°53'$) with three cleavages, that in one direction being highly perfect. D 4·39, H $2\frac{1}{2}$. Analysis III, by R. MAUZELIUS, gives the formula $PbCa_2(SiO_3)_3$. The mineral is readily and completely soluble in dilute nitric acid. It is perhaps a member of the pyroxene group.

Thaumasite from Långban is described as loose aggregates of small but distinct crystals. These are hexagonal with prismatic habit, $a:c=1:0{\cdot}9479$. L. J. S.

Minerals in the Crystalline Limestone of Crestmore, California. ARTHUR S. EAKLE (*Bull. Dep. Geol. Univ. California*, 1917, **10**, 327—360).—At Crestmore, in Riverside County, two hills of crystalline limestone, resting on a boss of granodiorite and intruded by veins of quartz-monzonite-porphyry and pegmatite, are extensively quarried for the manufacture of Portland cement, the partly decomposed granodiorite (anal. I) being used as a substitute for clay. In one hill the limestone is a white marble (anal. II), whilst in the other it is composed largely of blue calcite. In the latter, the metamorphic processes have been more intense, there having also been hydrothermal action by phosphatic, siliceous, and carbonated solutions, and zones composed of a great variety of metamorphic minerals have been developed at the contacts with the intrusive veins. The blue calcite, which forms bands and patches intermixed with the metamorphic minerals, is sometimes of a deep colour, fading on exposure to sky-blue. It is decolorised at a low heat, and the colour is thus perhaps due to organic matter. Detailed descriptions are given of about fifty mineral species from this locality, and analyses of the following. Wilkeite (A., 1914, ii, 283) and xanthophyllite (A., 1916, ii, 443) have been previously described.

Brucite (anal. III) forms grey, yellow, or red granules embedded in the white limestone. It consists of an aggregate of twisted plates and threads much compressed and strained, and has no doubt been derived from periclase (MgO) with an accompanying considerable ($2\frac{1}{2}$ times) increase in volume. Wollastonite is of abundant occurrence as columnar and fibrous masses; as snow-white, finely granular and loosely coherent aggregates (anal. IV); and as crystals of various types (anal. V of clear crystals). The distribution of the faces on these crystals indicates that the symmetry is monoclinic-hemimorphic, or perhaps triclinic. Several new crystal-forms are noted. The mineral is strongly triboluminescent. Refractive indices, $\alpha=1{\cdot}614$, $\beta=1{\cdot}629$, $\gamma=1{\cdot}631$. Idocrase as yellow or brown crystals and masses is also abundant; anal. VI, by J. B. WRIGHT, of green idocrase. Garnet, crystals and massive, of a cinnamon colour occurs with the idocrase; anal. VII by J. B. WRIGHT, of massive grossularite. A new analysis (VIII by

G. Surr) is given of the monticellite which occurs in intimate association with the xanthophyllite.

Two new species, crestmoreite and riversideite, hydrated calcium silicates, are described. *Crestmoreite* is an alteration product of wilkeite, and in the description of this mineral it was provisionally referred to as okenite (A., 1914, ii, 283). It occurs as small patches of earthy to compact, snow-white, and opaque material in the blue calcite. Under the microscope, it shows straight extinction with positive elongation, low birefringence, and $\beta=1{\cdot}590$. Hardness 3. It is readily soluble in acid with separation of some flocculent silica, although most of the silica goes into solution. Boiling water extracts some calcium. Water is expelled mostly at a high temperature; at 200° the loss is 3·27%, and at 300° 10·27%. From the analyses IX*a*—*c*, a complex formula is deduced, but the phosphate, sulphate, and carbonate no doubt represent admixed unaltered wilkeite. Simpler formulæ are $CaSiO_3,H_2O$ and $4H_2CaSiO_4,2H_2O$, preference being apparently given to the former.

Riversideite occurs as narrow seams of white, fibrous material in massive idocrase. H = 3; refractive indices, $\alpha=1{\cdot}595$, $\gamma=1{\cdot}603$; the fibres give straight extinction with positive elongation. A complex formula is deduced from anal. X; neglecting phosphate and sulphate, simpler formulæ are $2CaSiO_3,H_2O$ and

$$6H_2Ca_2Si_2O_7,H_2O,$$

preference being given to the former. These two new minerals may be regarded as hydro-wollastonites.

Orthoclase, pure white material from the pegmatite, anal. XI. Okenite (anal. XII, by W. Foshag) occurs as tufts of long, slender needles and fibres on apophyllite, which is found in cavities in wollastonite between the pegmatites and the limestone. The crystals are probably orthorhombic, $n=1{\cdot}55$. Prehnite occurs in cavities in the felspar of the pegmatites; in addition to the usual green drusy type, there is also a pale brown to colourless type, which forms crystals or, more often, compact, granular masses. Anal. XIII of the brown prehnite. Laumontite (anal. XIV) as columnar and fibrous masses occurs on the green prehnite.

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	P_2O_5.	SO_2.	CO_2.	H_2O.	Total.	Sp. gr.
I.	60·60	16·61	5·03	—	7·93	2·08	—	—	4·79		97·08*	—
II.	4·15	1·20		—	50·78	2·50	—	—	40·60		99·58	—
III.	—	—	0·55	—	—	67·48	—	—	—	31·73	99·76	2·39
IV.	51·77	—	2·12	—	44·85	—	—	—	—	1·02	99·76	—
V.	50·42	—	0·51	—	48·29	0·60	—	—	—	0·07	99·89	—
VI.	36·88	17·61	3·11	0·46	33·27	4·73	—	—	—	0·61	99·57†	3·36
VII.	35·53	21·11	3·95	0·60	36·06	0·78	—	—	—	1·23	100·15‡	3·39
VIII.	37·46	—	—	2·94	35·14	25·32	—	—	—	—	100·86	3·078
IX*a*.	36·12	—	—	—	42·71	—	2·38	2·42	1·16	14·98	99·77	—
IX*b*.	38·30	—	—	—	41·20	—	3·50	1·25	—	15·17	99·42	—
IX*c*.	34·42	—	—	—	43·54	—	3·50	2·24	—	16·24	99·42	—
X.	41·26	—	—	—	44·58	—	3·84	1·84	—	8·11	99·63	—
XI.	64·54	20·86	trace	—	1·86	trace	—	—	—	0·52	100·81	2·54
XII.	56·17	—	—	—	26·10	—	—	—	—	16·83	99·10	2·206
XIII.	44·10	24·20	—	—	25·20	—	—	—	—	5·86	99·36	—
XIV.	53·49	22·01	—	—	10·80	trace	—	—	—	13·39	99·69	—

* Alkalis not determined. † Incl. MnO 1·50, CuO 1·06, Na_2O 0·61.
‡ Incl. CuO 0·70, Na_2O 0·20. § Incl. K_2O 11·85, Na_2O 1·18.

L. J. S.

Two New Zircon Minerals—Orvillite and Oliveiraite. T. H. Lee (*Amer. J. Sci.*, 1919, [iv], **47**, 126—132; *Revista da Sociedade Brasileira de Sciencias, Rio de Janeiro*, 1917, No. 1, 31—38).—The zirconia-bearing rock or ore ("*caldasite*") of the Caldas region in Minas Geraes, Brazil, consists at times mainly of baddeleyite, containing ZrO_2 92%. One variety, in which the cavities are lined with small crystals of zircon, consists of a mixture of zircon and a new zirconium silicate, the latter being soluble in a mixture of hydrofluoric and hydrochloric acids. Analyses I and II are of the mixture, and III of material picked out under the microscope. The last corresponds with the formula

$$8ZrO_2,6SiO_2,5H_2O,$$

and for this the name *orvillite* is proposed.

	ZrO_2.	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	H_2O.	Total.
I.	71·88	25·31	0·62	0·15	—	0·43	1·56	99·95
II.	85·01	9·63	1·52	—	3·57	—	—	99·73
III.	68·04	25·45	—	—	—	—	6·35	99·72

The second mineral—*oliveiraite*—occurs with euxenite (anal. IV) at Pomba, Minas Geraes. Most of the euxenite crystals are coated with a yellow crust (anal. V). An analysis (VI) is also given of another euxenite, from Espirito Santo, which was supposed to contain a new element. The oliveiraite is greenish-yellow with a radially fibrous structure; analysis VII corresponds with

$$3ZrO_2,2TiO_2,2H_2O.$$

	Ta_2O_5.	Cb_2O_5.	ZrO_2.	TiO_2.	UO_2.
IV.	1·46	36·39		25·00	10·06
V.		52·51	—	25·00	4·93*
VI.	3·20	28·70	4·23	23·70	7·50
VII.	—	—	63·36	29·92	—

	Ce_2O_3.	Y_2O_3.	PbO.	H_2O.	Total.
IV.	0·46	23·08	0·14	2·41	99·00
V.	7·40		—	11·14	100·98
VI.	—	23·12	0·14	6·41	100·12†
VII.	—	—	—	6·48	99·76

* UO_3. † Including iron oxide 3·12, SnO_2 trace.

L. J. S.

Analytical Chemistry.

Approximation in the Calculation of Chemical Analyses. G. Panebianco (*Gazzetta*, 1918, **48**, ii, 189—206).—Independently of experimental errors, the accuracy of analytical results is limited to two or three figures by the fact that the atomic weights of the

elements are exact to at most four, and more usually only three, figures. Various examples are considered, the values taken for the atomic weights and their absolute errors being those of the international table for 1911. Since Sb = 120·2 and S = 32·07, the percentages of these two elements in antimonite are 71·417 and 28·582 respectively. If, however, the values $120·2 \pm 0·3$ and $32·07 \pm 0·01$ are employed in the calculation, the limiting percentages for the antimony are 71·730 and 71·106, the absolute error being 0·5 (71·730—71·106); similarly, for the sulphur, the absolute error is 0·06%. Hence the percentage of antimony is accurate to only two figures, namely, 71, and that of sulphur to three figures, namely, 28·5.

The relative error, E, of an atomic or molecular weight may be expressed in the form of a fraction with 1 as numerator and some multiple of a power of 10 as denominator, that is, $1/h \cdot 10^n$. If, then, the value of this fraction is known relatively to an approximate number, of which the first significant number to the left is p, this number will have n figures exact if h is equal to or less than p, or $(n+1)$ figures exact if h is greater than p. Thus, for antimony with the atomic weight 120·2 and an absolute error e equal to 0·3, $E < 1/4 \cdot 10^2$; for antimony trisulphide, $E < (2 \times 0·3 + 3 \times 0·1)/(2Sb + 3S) = 0·63/333·61 < 1/5 \cdot 10^2$. Further,

$$\text{for } 100\ 2Sb/(2Sb + 3S),\ E_1 < E_1 + E = 1/4.10^2 + 1/5 \cdot 10^2 = 9/20 \cdot 1/10^2 < 1/2.10^2,$$

and since 100 2Sb/(2Sb + 3S) = 71·417 and 2 is less than 7, only two digits, namely, 71, are accurate; similarly, for the percentage of sulphur, three digits are accurate.

A table is given showing for the atomic weights of the elements the absolute and relative errors. None of the latter is greater than $1/10^2$, and since for a compound the relative error must be less than the greatest of the relative errors of its constituent elements, such relative error of the molecular weight may be less than $1/10^2$.

The number of accurate digits in the percentages of the constituent elements of a compound may be rapidly established without calculation by application of the rule stating that the number of accurate digits of a quotient or product is one less than that of the term with the least number of accurate digits. Since no atomic weight has more than four digits exact, the percentage of any element or group of elements in a compound cannot have more than three digits accurate; further, such percentage cannot have less than two digits accurate (see above).

These considerations are extended by taking into account the weight of substance taken for analysis and the sensitiveness of the balance, the calculation of the error being employed to determine the minimum quantity of substance necessary to give the maximum accuracy in the digits of the percentage composition. T. H. P.

The Estimation of Solutions of Hydrochloric Acid and of Ammonia by Weighing Ammonium Chloride, and the Volatilisation of this Salt at Different Temperatures. Victor Auger (*Bull. Soc. chim.*, 1918, [iv], **23**, 467—472).—A reply to Villiers (compare A., 1918, ii, 332). W. G.

Estimation of Phosphorus and Silicon in Cast Iron. Alfredo Cavazzi (*Annali Chim. Appl.*, 1918, **10**, 137—149).—The method of estimating phosphorus in cast iron (A., 1917, ii, 540) has been simplified in many of its details. The mixture of ferric sulphate with silica and carbon, separated as described, is boiled for about thirty minutes with dilute nitric acid (1:5) in a beaker over which is placed a retort containing cold water to act as a reflux condenser. The solution of ferric sulphate is filtered, the residue washed with water, acidified with nitric acid, and the orthophosphoric acid in the filtrate precipitated by means of ammonium molybdate. The precipitate is washed, dissolved, re-precipitated, and dissolved in ammonia solution, as described in the original method, and the solution is boiled with 3 grams of sodium chloride in order to precipitate any remaining iron as ferric phosphate. The precipitate is washed with boiling sodium chloride solution and fused with alkali carbonates, the mass treated with boiling water and filtered, and the filtrate acidified with nitric acid, treated with ammonia in slight excess, and added to the main solution. The phosphoric acid is then precipitated with magnesia mixture. The silica is estimated in an aliquot portion of the residue of carbon and silica by ignition over a blowpipe flame in a platinum crucible. [See also *J. Soc. Chem. Ind.*, 1919, March.] C. A. M.

Estimation of Arsenic in Ferro-molybdenum and other Alloys. O. Binder (*Chem. Zeit.*, 1918, **42**, 619).—The estimation of arsenic in ferro-molybdenum and similar alloys may be accelerated by carrying out all the operations in a long-necked Kjeldahl flask. The alloy is dissolved in nitric acid, the solution heated with sulphuric acid until acid fumes no longer appear, and then diluted, and the arsenic distilled from the same flask in the form of arsenious chloride. C. A. M.

Accurate Estimation of Carbon Monoxide in Gas Mixtures. J. Ivor Graham (*J. Soc. Chem. Ind.*, 1919, **38**, 10—14T).—The author's experiments show that methods of estimation of carbon monoxide based on the reaction $5CO + I_2O_5 = 5CO_2 + I_2$ are capable of yielding exceedingly accurate results if certain precautions are observed. Two modes of procedure are adopted for the routine estimation of this gas, according as (*a*) the carbon monoxide content exceeds 0·2% and an accuracy of 0·02% is sufficient, or (*b*) the carbon monoxide content is about, or less than, 0·2% and a greater degree of accuracy than 0·02% is required. For the

analysis of samples as under (*a*), the apparatus described by the author and Winmill (T., 1914, **105**, 1996) is modified, mainly by replacing the beaker of water used for heating purposes by a small steam-bath, all burette readings being taken with the U-tube at the constant temperature of the steam-bath. Descriptions and sketches are given of the apparatus and of a portable form capable of estimating very much smaller quantities of carbon monoxide accurately to within less than 0·01%. The latter apparatus is varied slightly according as it is to be used in safety pits or in "naked-light" pits or other places. T. H. P.

Rapid Organic Combustions of Substances containing Nitrogen. Harry L. Fisher and A. H. Wright (*J. Amer. Chem. Soc.*, 1918, **40**, 868—869).—Reimer (A., 1915, ii, 578) has used cerium dioxide as a catalyst in the combustion of organic substances; cupric oxide is also employed, and, by the addition of lead peroxide and minium, carbon and hydrogen can be estimated in substances containing nitrogen. To prevent formation of cupric nitrate, the layer of cupric oxide must be maintained at a dull red heat; the lead peroxide–minium mixture is placed in the combustion tube about 5 cm. beyond the cupric oxide, and is heated at 300—320°. Several successive combustions may then be made in the same tube without changing the cupric oxide. W. P. S.

Methods of Water Analysis. Atilio A. Bado, Victor J. Bernaola, Aurelio F. Mazza, and Leopoldo Dasso (*Obras Sanitarias de la Nación, Buenos Aires*, 1918, 98 pp.).—A monograph giving a detailed account of the chemical and microbiological analytical methods in use in the Laboratorio de Análisis de Aguas y Ensayos de Materiales de las Obras Sanitarias de la Nación of Buenos Aires for the examination of potable waters. W. S. M.

Rapid Method of Reduction of Potassium Platinichloride. Horsch (*Compt. rend.*, 1919, **168**, 167—169).—In the estimation of potassium, the precipitate of potassium platinichloride, after being well washed with 80% alcohol, is dissolved in boiling water and the solution transferred to a weighed platinum crucible. Two to three c.c. of alcohol are added, and the whole heated on a rapidly boiling water-bath for twenty-five minutes, after which a few more drops of alcohol are added and the heating continued for five minutes. In this way, the platinum is deposited gradually and uniformly on the interior surface of the crucible, and is quite adherent. The liquid is poured out, the deposit washed with water, and the crucible is dried, ignited, and weighed. During the ignition, the deposit turns from black to a shiny, metallic appearance, and remains adherent. For the process, it is essential to use a platinum crucible, as the reduction only takes place in the presence of platinum, and the concentration of the potassium platinichloride solution must not exceed 0·25—0·30%. W. G.

Gravimetric Analysis. IX.—XI. Estimation of Calcium in the Presence of Phosphoric, Arsenic, and Boric Acids. L. W. WINKLER (*Zeitsch. angew. Chem.*, 1919, **32**, i, 24).—Calcium is precipitated quantitatively as oxalate in solutions containing phosphoric, arsenic, and boric acids provided the solution is hot and that acetic acid and ammonium chloride are present. The following procedure is recommended. About 50 c.c. of solution, containing not more than 0·1 gram of calcium, are made slightly alkaline by the addition of ammonia, drop by drop. The solution is diluted to 100 c.c., and 3 grams of ammonium chloride added and allowed to dissolve; the solution is then acidified with 10 c.c. of *N*-acetic acid, and the calcium is precipitated as oxalate as prescribed for the pure solution. The last traces of precipitate may be removed from the beaker by means of a little pure methyl or ethyl alcohol, which is then poured on to the edges of the filter so as to wash them. The result may be corrected by a blank using a pure calcium salt. If a considerable portion of arsenic or phosphoric acid is present, a double precipitation is desirable, the first precipitate being allowed to remain overnight, collected, washed with ammonium oxalate solution, ignited, the residue dissolved in hydrochloric acid, and the calcium oxalate reprecipitated as before. A. B. S.

Rapid Estimation of Lead in Brass and Alloys. G. H. HODGSON (*Chem. News*, 1919, **118**, 37—38).—A gravimetric and a volumetric method for the rapid estimation of lead in brass and similar alloys are described. The gravimetric method consists in precipitation of the lead as chromate from an acetic acid solution, conversion into sulphate, and finally weighing as molybdate. Five grams of the alloy are dissolved in 25 c.c. of nitric acid (D 1·4), the solution diluted with 200 c.c. of water, and sufficient aqueous ammonia (20 c.c., D 0·880) added to precipitate all the copper. Sufficient 80% acetic acid is then added to produce a clear, slightly acid solution, and 10 c.c. of 3% potassium dichromate are added, the mixture shaken, and kept for one hour. The precipitated lead chromate is filtered on a paper pulp pad and washed to remove the copper; hot douches of 30% sulphuric acid are poured on to the pad until the precipitate is entirely white. The sulphate is then washed with water. The lead sulphate is now dissolved by pouring about 40 c.c. of hot ammonium acetate solution containing acetic acid through the filter. The solution is raised to the boiling point and treated with ammonium molybdate. The precipitate is allowed to settle, filtered through an ashless paper pad, washed with water containing a little ammonium acetate, ignited, and weighed as lead molybdate. The whole process may be completed in four hours. The volumetric process consists in precipitation of the lead as chromate, as described above; the chromate precipitate is washed with water and warm dilute acetic acid (5%) until free from copper and the excess of potassium chromate. The chromate is dissolved by pouring 1:4 hydrochloric acid on to the

precipitate, and the pad finally washed with water to wash all chromic acid through. The free chromic acid may be estimated by titration with $N/10$-ferrous ammonium sulphate solution or by adding 10 c.c. of 10% potassium iodide solution and titrating the liberated iodine with $N/10$-sodium thiosulphate solution. The whole process may be carried out in two hours. Both methods have been compared with the gravimetric sulphate method, and found to give results in excellent agreement with those obtained by the better known method. J. F. S.

Unification of Methods for the Analysis of Cast Iron and Steel. A. Marinot (*Ann. Chim. anal.*, 1919, [ii], **1**, 5—10).—The following methods are suggested as being trustworthy. Total carbon may be estimated by Wiborg's method (combustion with sulphuric acid and chromic acid), by the ordinary method of combustion, or by the method described by Mahler and Goutal (A., 1912, ii, 807). Manganese is estimated by Traver's method (A., 1917, ii, 511), and phosphorus by the molybdate method. Sulphur is liberated as hydrogen sulphide in an atmosphere of carbon dioxide, collected in zinc acetate solution, and estimated iodometrically. Arsenic is also estimated iodometrically after distillation. [See, further, *J. Soc. Chem. Ind.*, March.] W. P. S.

Direct Estimation of combined Ferric Oxide in Silicates Insoluble in Acids. O. Hackl (*Chem. Zeit.*, 1919, **43**, 9).—Knecht's volumetric method of estimating ferric salts by titration with titanous chloride, using potassium thiocyanate as indicator, is not directly applicable to silicates which have been decomposed with hydrofluoric acid. The influence of a small amount of this acid in preventing the appearance of the colour reaction with thiocyanate may be obviated by dissolving boric acid in the solution. This also restores the colour of ferric thiocyanate which has been destroyed by hydrofluoric acid; or methylene-blue, the colour of which is not affected by traces of hydrofluoric acid, may be used as indicator in place of potassium thiocyanate. C. A. M.

Estimation of Molybdenum. Kuno Wolf (*Zeitsch. angew. Chem.*, 1918, **31**, i, 140).—When molybdenum is separated as its sulphide, and the latter then converted by ignition into molybdenum trioxide and weighed, the temperature during the ignition should not exceed 425°. The conversion of the sulphide into trioxide is complete at 400°; no further change takes place between 400° and 450°, but above 450° the trioxide sublimes. The correct temperature (400—425°) is most readily attained by using an electric furnace. W. P. S.

Emanation Method of Estimating Thorium. G. H. Cartledge (*J. Amer. Chem. Soc.*, 1919, **41**, 42—50).—It is shown by circulating a current of air through a thorium solution and an ionisation chamber until the activity has become constant

that the thorium content of any substance, which can be dissolved completely, may be estimated with an error which is not greater than 1·5%. In making the determination, it is advisable to draw air through the solution for some minutes, before connecting to the ionisation chamber, for the purpose of removing any radium emanation which may be present. It is also essential that the dimensions of the apparatus used should be the same in all experiments and that the temperature should be as nearly as possible the same. The method has been tested with a specimen of monazite sand, and it is found by this method that 8·61% of thorium oxide is present, whereas the gravimetric analysis indicates 8·57%. Details are given of a method of preparing a solution of monazite for this analysis. Two notes on the gravimetric analysis of monazite are appended to the paper. Carney and Campbell (A., 1914, ii, 583) use ammonium perchlorate and sulphuric acid for the destruction of the filter paper and the conversion of thorium pyrophosphate into thorium sulphate. This process may be carried out in one-half the time by using sulphuric acid and fuming nitric acid (D 1·53) instead. It is shown that the practice of using a slightly turbid, unfiltered solution of monazite in the analysis leads to high thorium results, since the titanium oxide is weighed along with the thorium. J. F. S.

Estimation of Gold, especially in Animal Tissues. Sidney M. Cadwell and Gladys Leavell (*J. Amer. Chem. Soc.*, 1919, **41**, 1—12).—With the object of finding a method capable of estimating the amount of gold present in tissues, the authors have investigated the methods available for the estimation of gold, and have devised a method which, with a maximum error of 0·05 mg., is capable of estimating amounts of gold of 3·0 mg. and less. This method was required in connexion with the gold salt treatment of tuberculosis, and consists in placing 10 grams of fresh tissue in a 300 c.c. Kjeldahl flask, adding 10 c.c. each of concentrated sulphuric and nitric acids, and digesting over a free flame until the cooled solution is colourless. Air is then blown into the flask, and the mixture again heated until the volume of solution is reduced to 2 c.c.; this procedure removes most of the sulphuric acid. One c.c. each of hydrochloric and nitric acids is then added and the mixture boiled for a few minutes, and then a further c.c. of hydrochloric acid added. The solution is cooled, diluted with 5 c.c. of water, and concentrated ammonium hydroxide added until the colour is discharged, and then an excess of 2 c.c. The mixture is boiled, and the white precipitate which forms at this point dissolved by adding 5 c.c. of concentrated hydrochloric acid and boiling for three minutes. The solution is filtered through asbestos on an alundum plate, and the filtrate treated with ammonium hydroxide until it smells distinctly of ammonia. The volume of the solution should be now about 40 c.c.; 1·1 c.c. of 85% phosphoric acid and 0·75 gram of disodium hydrogen phosphate are added, and the solution electrolysed. A rotating anode and a cathode of

platinum sheet are used. The difference of electrode potential should be 0·9—1·2 volts, and the most efficient temperature is 60°. The method has been slightly modified to allow of its use for larger quantities of gold. By the addition of 6 grams of ammonium chloride to prevent precipitation, 30 to 40 mg. of gold can be electrolysed at 60°, with a voltage of less than 0·6 volt for the first thirty to forty-five minutes and below 1·3 volts for the remainder of the time, complete deposition usually requiring one and a-half hours. Under the conditions stated, gold can be completely separated from equivalent amounts of copper and iron, but the time required for electrolysis is greater than when these substances are not present. It makes very little difference whether the electrolysed solution is neutral or much more acid than stated above. The average time required for carrying out a complete analysis of gold by this method is less than two hours. J. F. S.

Quantitative Estimation of Sugar. A New Apparatus for the Estimation of Sugar in Urine. H. Citron (*Münch. med. Woch.*, 1918, **65**, 1053; from *Chem. Zentr.*, 1918, ii, 869).—The author describes a simple apparatus for the estimation of sugar in urine according to Bang's method. H. W.

Quantitative Colorimetric Estimation of Pentosans in Meal. G. Testoni (*Staz. sper. agr. Ital.*, 1917, **50**, 97—108; from *Chem. Zentr.*, 1918, ii, 865—866).—The method of Tollens and Krueger gives high results, because the starch is slowly but continuously converted into furfuraldehyde. Sucrose, maltose, and dextrose when heated with hydrochloric acid of the prescribed concentration also yield distillates from which phloroglucides are obtained. The hexoses, starch, and cellulose cause incorrect results in the estimation of methylpentosans, since, when treated with dilute mineral acid, they give, as intermediate product, ω-hydroxymethylfurfuraldehyde, which yields a phloroglucide, m. p. 95°, soluble in alcohol.

The author has therefore endeavoured to find a process by which the pentosans can be converted into pentoses easily identified by colour reactions, whilst the other constituents of the meal are not attacked in a vitiating manner. The most suitable reagent is a mixture of acetic acid (90 c.c.) and concentrated hydrochloric acid (D 1·19, 10 c.c.) at 45—50°. On addition of 0·25% phloroglucinol to this mixture, a red solution is obtained, which remains clear even when diluted with one hundred times its volume of water, and has well-marked absorption bands in the red, yellow, and blue. Different varieties of starch, dextrins, and different sugars have no influence on the reaction, whilst pentoses alone and in artificial mixtures are quantitatively found. The pentosans, even those contained in clover, are completely hydrolysed when heated for forty-five minutes with the reagent. H. W.

Action of Potassium Cyanide on Ammoniacal Copper Sulphate and its Application to the Estimation of Hydrocyanic Acid and Copper. L. Jennesseaux (*Ann. Chim. anal.*, 1919, [ii], **1**, 15—20).—Lassaigne's test for hydrocyanic acid (form-

ation of a white precipitate when a cyanide solution is treated with a drop of copper sulphate solution, then with sodium hydroxide solution, and the mixture acidified with sulphuric acid) may be rendered more sensitive if the copper sulphate solution is first treated with sodium hydrogen sulphite in quantity sufficient to change the colour from blue to green. When potassium cyanide solution is added to ammoniacal copper sulphate solution, a crystalline precipitate forms having the composition

$$2Cu_2(CN)_2,Cu(CN)_2,4NH_3.$$

Further addition of cyanide then causes the solution to become colourless, and the precipitate dissolves. This point is reached when a definite proportion of cyanide has been added, and the reaction may be used for the estimation of hydrocyanic acid, and, conversely, of copper. The copper sulphate solution used should contain 4·99 grams of the crystallised salt per 100 c.c., and this solution is mixed with 80 c.c. of $N/1$-ammonia and 20 c.c. of water; 10 c.c. of the mixture is a convenient quantity to take for an estimation. [See, further, *J. Soc. Chem. Ind.*, 1919, March.]

W. P. S.

Opium Analysis. D. B. Dott (*Pharm. J.*, 1918, **101**, 318).—The author deals with certain criticisms by Annett and Singh (A., 1918, ii, 279) on the British Pharmacopœia method for the assay of opium by the lime-water process. Whatever may be the solvent influence of codeine on morphine in aqueous solution, the conditions of the assay process are entirely different, in that sufficient ether is added to hold in solution all the codeine possibly present. Moreover, the author has checked the alternative method proposed (*loc. cit.*), consisting in shaking the lime-water solution of the alkaloids with toluene to remove the codeine before precipitating the morphine by the official process. This alternative method (using benzene instead of toluene) gave a morphine precipitate heavier in weight and showing a higher titration value, but obviously less pure than the morphine prepared by the standard method. When the impurities were removed by washing with 80% alcohol saturated with morphine, the morphine prepared by the new process was no more than that prepared by the Pharmacopœia process, and there is no reason for altering the latter in the direction indicated by Annett and Singh. J. F. B.

Separation and Estimation of Uric Acid and other Purines in Urine. F. Telle (*Bull. Sci. Pharmacol.*, 1918, **25**, 208—211; from *Chem. Zentr.*, 1918, ii, 770).—The uric acid is precipitated by the addition of solid ammonium chloride and ammonia to the acid urine, and, after collecting on a small filter, estimated by titration with permanganate in the presence of sulphuric acid. The purines in the filtrate are estimated by Denigès's method.

H. W. B.

Quick Estimation of Albumin (in Urine). A. Simon and C. Pagel (*Bull. Sci. Pharmacol.*, 1918, **25**, 204—208; from *Chem. Zentr.*, 1918, ii, 767).—The urine is treated with saturated sodium

sulphate solution and two or three drops of acetic acid, and is then heated until the albumin separates in flocks. By means of the diaphanometer described in the original paper, the height of the liquid is determined at which a line drawn on the bottom of the vessel is no longer discernible. The amount of albumin in the urine can then be read off from the accompanying table. H. W. B.

Estimation of Urobilin in Urine. S. Marcussen and Svend Hansen (*J. Biol. Chem.*, 1918, **36**, 381—389).—The presence of urobilin in urine may be readily detected by the following modification of Schlesinger's test. One gram of zinc acetate is weighed into a test-tube, and 10 c.c. of absolute alcohol are then added; 10 c.c. of the urine are placed in another test-tube, to which are added three drops of a 5% alcoholic solution of iodine. The contents of the two test-tubes are then mixed by repeated decantations until all the zinc acetate has dissolved. After filtering off the precipitate, the filtrate is found to be fluorescent if urobilin or urobilinogen was originally present in the urine.

By diluting the urine until fluorescence is no longer obtainable, a rough idea is furnished of the quantitative relationship of the urobilin. H. W. B.

The Estimation of the Nuclein Content of Yeast. C. A. Lubsen (*Pharm. Weekblad*, 1918, **55**, (50), 1625—1628).—The hydrolysis of nucleoproteins by hydrochloric acid–pepsin solutions yields soluble albumins and an insoluble residue of nucleins; the latter contain 4—7% of phosphoric acid, representing the whole of the phosphorus present in the nucleoprotein. Further hydrolysis, for example, by trypsin, yields another albumin group, together with a nucleic acid. In analysing foodstuffs for nuclein content, Jebbink employs the pepsin–hydrochloric acid hydrolysis, using a solution containing 0·24% HCl, and determines the phosphorus in the insoluble residue of nuclein, using this as a measure of the nuclein content. Grijns criticises this method on the ground that so strong a solution of hydrochloric acid would cause further hydrolysis of the nuclein to the soluble nucleic acid, thus leading to low results.

The author has examined the question by carrying out experiments with yeast, using pepsin–hydrochloric acid solutions containing various proportions of hydrogen chloride. He finds that the weak solution (0·1% HCl) recommended by Grijns gives low results, owing to the slowness of the hydrolysis, whereas Jebbink's solution (0·24% HCl), and even stronger solutions (0·35% HCl), gives accurate results. It is therefore clear that the nucleins are not further hydrolysed by acid solutions of this strength, and Grijns's contention appears to have been wrongly based on the assumption that hydrolysis proceeded to the soluble nucleic acids. S. I. L.

General and Physical Chemistry.

Reversal of Spectrum Lines Produced by a Spark under Water. Toshikazu Mashimo (*Mem. Coll. Sci. Kyoto. Imp. Univ.*, 1918, **3**, 73—79).—The spectra of aluminium, zinc, cadmium, and mercury, produced by sparking between poles of these metals under water, have been examined down to $\lambda = 1850\ \mu\mu$. It is shown that certain of the lines are reversed by this process; in the case of aluminium the lines λλ 1930, 1935, 2205, 2210, 2263, 2268, 2367, 2378, 2567, 2575, 2653, 2661, 3082, 3093, and 3944 $\mu\mu$ are reversed. With zinc the lines λλ 2026, 2062, 2087, 2097, 2102, 2105, 2139, 2288, and 2832 (?) suffer reversal. Cadmium gives the lines λλ 2144, 2288, 3069, and 3095 $\mu\mu$ reversed, whilst in the case of mercury the lines λλ 2482 and 2537 $\mu\mu$ are reversed. J. F. S.

Effect of an Electric Field on the Spectrum Lines of Helium. II. Toshio Takamine and Noboru Kokubu (*Mem. Coll. Sci. Kyoto. Imp. Univ.*, 1918, **3**, 81—92. Compare A., 1917, ii, 401).—Making use of Lo Surdo's method, the effect of electric fields (3000—70,000 volt per cm.) on the helium lines λλ 4169, 4144, 4026, 4009, 3965, 3868, 3830, 3820, 3614, 3448, and 2945 has been examined and the results compared with those of Stark, Brunetti, and Koch. It is shown that helium lines are effected in three ways by an electric field, (1) symmetrical resolution (λ 4686), (ii) non-symmetrical resolution (diffuse series of lines of helium and parhelium), (iii) one-sided displacement (principal series lines and sharp series lines of helium and parhelium). In the last-named case only the lines belonging to the principal series of parhelium are displaced toward the violet, whilst the other three series lines are displaced toward the red. Diffuse series lines are usually accompanied by an isolated component on the violet side, the starting point of which approaches more nearly to the initial line as the term number increases. The line λ 3830, the position of which was calculated by Koch, but not observed by him, appears in the photographs of some of the present experiments. Two lines, λ 2804 and 2482 A.U., which are probably due to mercury, were also found to be displaced slightly towards the red in an electric field. J. F. S.

Investigation of Extreme Ultra-violet Spectra, with a Vacuum-grating Spectrograph. J. C. McLennan and R. J. Lang (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 258—273).—A preliminary paper, in which a full description of a vacuum-grating spectrograph designed and made by the Adam Hilger Company is given. The theory of the concave grating is developed, and the experimental details for determining wave-lengths by means of this instrument are described. A short summary of the previous work in the extreme ultra-violet region precedes a description of the various

types of arcs used in the present examination of the extreme ultra-violet spectra of mercury, copper, iron, and carbon. The spectra were photographed on Schumann plates made by Hilger, and the wave-lengths are measured to within one Ångstrom unit. In the case of mercury nine lines appear in the photograph, lying between $\lambda=2054$ Å.U. and $\lambda=1435$ Å.U.; with copper thirteen lines appear between $\lambda=2243$ Å.U. and $\lambda=1925$ Å.U.; in the case of iron twenty-seven lines are found between $\lambda=2027$ Å.U. and $\lambda=1427$ Å.U.; carbon shows twenty-eight lines between $\lambda=2023$ Å.U. and 584 Å.U. Photographs of all the spectra are reproduced in the paper. J. F. S.

Emission and Absorption in the Infra-red Spectra of Mercury, Zinc, and Cadmium. Raymond C. Dearle (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 280—299).—The absorption spectra of mercury, zinc, and cadmium have been measured in the infra-red region; for the region up to 8500 Å. the spectrum was photographed, whilst above this wave-length a linear thermopile and galvanometer were used. The light was obtained from a mercury amalgam lamp of the Heraeus type; the amalgam consisted of 60% mercury, 20% lead, 20% bismuth, ½% zinc, and ½% cadmium. In some cases an arc of the metal in a vacuum was employed. For the energy measurements a 100 volt Nernst glower was used. In the case of mercury absorption bands $\lambda=1{\cdot}014\,\mu$, $1{\cdot}038\,\mu$, $1{\cdot}065\,\mu$, $1{\cdot}089\,\mu$, $1{\cdot}129\,\mu$, $1{\cdot}160\,\mu$, $1{\cdot}207\,\mu$, and $1{\cdot}359\,\mu$ were observed. Energy measurements were made in the region 1·2—1·5 μ, the only absorption band observed lying at $\lambda=1{\cdot}359\,\mu$. No absorption was shown in the case of the energy measurements of zinc until the temperature had been raised to 275°. At this temperature absorption was observed at $\lambda=1{\cdot}105$; in the longer wave-lengths evidence was more difficult to obtain, but indications of absorption were obtained at $\lambda\lambda$ $1{\cdot}379\,\mu$, $1{\cdot}41\,\mu$, $1{\cdot}57\,\mu$, and $1{\cdot}65\,\mu$. With cadmium vapour absorption was found at $\lambda=1{\cdot}040\,\mu$, which is the first line of the series $\nu=(2{\cdot}5S)-(m,P)$; a second strong absorption band occurs at $\lambda=1{\cdot}503\,\mu$, whilst less marked absorption occurs at $\lambda\lambda=1{\cdot}129\,\mu$, $1{\cdot}395\,\mu$, $1{\cdot}4475\,\mu$, $1{\cdot}522\,\mu$, and $1{\cdot}563\,\mu$. By the photographic method a line was observed at 6977·4 Å. in one series of experiments, but this line could not be reproduced. Some absorption experiments were carried out with a quartz cell containing cadmium iodide; it was found that there was no absorption in the visible and ultra-violet regions at comparatively low temperatures, but with increased temperature a broad band was observed which extended from the limit of the ultra-violet end of the spectrum up to a wave-length of about $\lambda=4000$ Å. Attempts to resolve this band failed. In the longer wave-lengths no absorption was visible at wave-lengths characteristic of the cadmium spectrum. Energy measurements made in the long wave-length region above $\lambda=1{\cdot}0\,\mu$ showed the presence of an absorption band at $\lambda=1{\cdot}040$ when the temperature of the cell was above that necessary for dissociation. The emission and absorption curves obtained by bombarding mercury vapour

with electrons with the object of producing the single line spectra are given. J. F. S.

Characteristic Ultra-red Vibrations of Diatomic Crystals. M. Born (*Physikal. Zeitsch.*, 1918, **19**, 539—548).—A mathematical paper, in which the relationship between the constants of a diatomic regular crystal grating is considered. The influence of electrons on the index of refraction in the ultra-red is also considered mathematically. The results obtained are applied to crystals of rock salt, sylvine, potassium bromide, potassium iodide, pyrites, fluorspar, and sodium chlorate. J. F. S.

Absorption Spectra and the Ionisation Potentials of Calcium, Strontium, and Barium. J. C. McLennan and J. F. T. Young (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 273—279).—The absorption spectra of calcium, strontium, and barium have been determined, and from the values of the wave-lengths the ionisation potential of these elements calculated. In the case of calcium a hollow carbon filled with metallic calcium was used, and it was observed that the reversals were confined entirely to those wave-lengths which were members of the series $\nu=(1{\cdot}5,S)-(m,P)$; as given by Lorenser (Inaug. Diss.) these are:

$m=$	2.	3.	4.	5.	6.	7.
$\lambda=$	4226·91	2721·77	3298·66	2275·60	2200·8	2151·00

$m=$	8.	9.	10.	11.
$\lambda=$	2118·99	2097·8	2083·2	2072·8

In the case of strontium the sulphide was employed instead of the metal, and the wave-lengths for $\nu=(1{\cdot}5,S)-(m,P)$ also accord with those of Lorenser. The following were found:

$m=$	2.	3.	4.	5.	6.
$\lambda=$	4607·52	2931·98	2569·60	2428·16	2354·40

$m=$	7.	8.	9.	10.	11.
$\lambda=$	2307·5	2275·5	2253·5	2237·4	2226·0

In the case of barium the oxide was used, and by noting the reversals nine members of the series $\nu=(1{\cdot}5S)-(m,P)$ were obtained; these are:

$m=$	2.	3.	4.	5.	6.
$\lambda=$	5535	3275	2845	2597	2542
$\nu=$	10864·6	30534·4	35149·4	38502·1	39339·1

$m=$	7.	8.	9.	10.
$\lambda=$	2498	2470	2455	2441
$\nu=$	40032	40486	40733·2	40966·8

From the limiting frequencies of the single series of the spectra the following ionisation potentials of the vapours have been calculated: mercury, 10·45 volts; zinc, 9·4 volts; cadmium, 9·0 volts; magnesium, 7·65 volts; calcium, 6·12 volts; strontium, 5·7 volts; and barium, 5·21 volts. J. F. S.

Changes in Spectrum Intensity and Weakening of the Iodine Fluorescence by means of a Magnetic Field. W. STEUBING (*Ann. Physik*, 1919, [iv], **58**, 55—104).—In a previous note (*Verh. deut. physikal. Ges.*, 1913, 1181) it was shown that when fluorescent iodine vapour is brought between the poles of a powerful electric magnet, the intensity of the fluorescent light is greatly diminished. The present paper deals with the investigation of this phenomenon. The light changes have been investigated spectrophotometrically and spectrographically, and a series of energy measurements have also been made. It is shown that it has been impossible to attribute the weakening of the iodine fluorescence to any definite cause, but that it depends on the action of a magnetic field on the electron vibrations which give rise to the emission of a band spectrum. The effect is greater with the higher frequencies than with the lower, and, further, the magnetic field has a more pronounced action the greater the vibration amplitude during the emission. The present phenomenon, therefore, has nothing in common with other processes which diminish or destroy fluorescence. The magnetic action has little to do with the actual fluorescence, and the same effect is to be expected if the same band spectrum is produced in some other way; it is to be expected that the magnetic weakening will take place more easily the greater the energy per molecule with which the emission occurs, and consequently an electrically produced spectrum will be correspondingly more strongly weakened by weaker magnetic fields. J. F. S.

The Magnetic Field and the High Frequency Spectrum of the Elements. RITA BRUNETTI (*Nuovo Cim.*, 1918, [vi], **16**, ii, 5—18).—Assuming that the action of a magnetic field results in decomposition of high frequency radiations, the results of the author's experiments show that the ordinary means of spectral analysis would be insufficient to reveal directly such decomposition, if the latter were of the type and order of magnitude of the Zeeman phenomenon. None of the theories on the emission of high frequency radiations excludes the possibility of a decomposition produced in this manner. The lines of the K spectrum for iron, nickel, and copper are found by the curved crystal method to be double, the mean difference between the two components being 8/1000 and 11/1000 Ångström units for the α and β lines respectively. No qualitative modification of any kind is exhibited in the characteristic spectra of these elements under the influence of magnetic fields of moderate magnitude and degree of variation. T. H. P.

Light Positive and Light Negative Photophoresis [in Connexion with] Sulphur and Selenium. IRENE PARANKIEWICZ (*Ann. Physik*, 1918, [iv], **57**, 489—518).—It has been shown by Ehrenhaft (*ibid.*, 1918, **56**, 81) that particles of matter fall under the action of gravity, but rise in an electric field; some particles when subjected to a strong beam of light are deflected, in the horizontal direction, from their original path. Thus sulphur particles

move in the direction opposite to that of the beam of light (light negative); selenium particles under some conditions move in the direction of the beam of light (light positive). The present paper is a continuation of this work, and deals with the dependence of the photophoresis on the chemical nature of the particles, the intensity of the light, pressure of the surrounding medium, and the size of the particles. The work has been carried out with sulphur and selenium particles of radius $8-60\times10^{-6}$ cm. The methods adopted in the investigation were similar to those employed by Ehrenhaft. It is shown that sulphur particles are always light negative, whereas selenium particles are either light negative or light positive, depending on the duration of heating in the production of the particles. The light negative photophoric force on selenium particles is approximately six times as great as the force of the same light beam on sulphur particles of the same mobility. The intensity, with which particles of a given material react on the light, is dependent on the size of the particles. The negative photophoresis shows its maximum action on sulphur particles of radius 27×10^{-6} cm., and on selenium particles of radius 15×10^{-6} cm. The photophoric force on sulphur and negative selenium is independent of the time, whilst with positive selenium it is a function of the time. The power of reaction on the light of positive selenium decreases with time. The photophoric force is independent of the surrounding gas and also of the pressure. The independence of the photophoric force on the pressure, the chemical nature of the surrounding gas, the decrease of the positive reaction of selenium particles which is due to an internal change of the selenium, and, further, the fact that particles of different materials, but of the same mobility, are very differently acted on by light, all tend to confirm the conclusion of Ehrenhaft that the action is a direct one of the light on the material. J. F. S.

X-Ray Spectra and the Constitution of the Atom. II. L. Vegard (*Phil. Mag.*, 1919, [vi], **37**, 237—280. Compare A., 1918, ii, 144).—A theoretical paper, in which the process of recombination of the primaries is discussed, together with some of the consequences which follow from them. Calculations are made of the quant-number and the number of electrons of the ring systems from the observed frequencies. The possibility of there being two *L* and two *M* rings is considered. It is shown that whether recombination is assumed from a normal or deformed primary system, or recombination from a secondary one, it must be assumed that the angular momentum of the electrons left behind in the atom remains unchanged; and further it must be assumed that the changes of energy of the systems situated between the broken ring and the ring of departure enter into the energy quantum of radiation which is emitted as the result of recombination. On the basis of the theory of the production of *X*-rays developed by the author it must follow that recombination takes place from secondary systems, and that always the angular momentum of the electrons left behind

in the atom is kept constant during expulsion and recombination. A number of relationships of the atomic constitution and properties of the atoms are given. All elements belonging to the same period of the periodic classification have the same quant-number, and this number increases by one unit on passing from one period to the next. J. F. S.

Radioactivity and the Coloration of Minerals. Edgar Newbery and Hartley Lupton (*Mem. Manchester Phil. Soc.*, 1918, **62**, No. 10, 1—15).—The colours obtained on exposing various substances to the action of the β- and γ-rays of radium, and sometimes to the α-, β-, and γ-rays of the radium emanation, are recorded. Various differently coloured fluorspars, owing to their wonderful range of colours and remarkable thermo-luminescence, proved the most interesting, the changes produced by radium being so varied as to be bewildering. A colourless Matlock fluorspar after twenty-four hours' exposure to 50 mg. of radium became blue, deeper than a copper sulphate crystal, the colour being permanent in the dark but destroyed by direct sunlight, or, more slowly, by daylight and by gentle heating, but the fluorspar may be recoloured by radium indefinitely. Under cathode rays, only a faint purple surface colour was produced. The blue colour is probably due to the γ-rays, as it penetrates right through the crystal. The thermo-luminescence was green and feeble, but a Pyrenean fluorspar, not coloured by radium, gave a remarkable and lasting green light on heating, even though only exposed 150 mm. away from the radium. The thermo-luminescence of Cornish chlorophane is to be ascribed to γ-rays from radioactive materials. On crystal quartz there was no sign of the "rotting" produced by radium rays in fused quartz. The natural colours are discharged by heating, but may be restored by radium.

Clear selenite crystals were coloured brown in regular figures, the remaining parts being colourless, a phenomenon which Miers explains by certain faces of the crystal during growth attracting impurities, to which the colour is to be ascribed. Among other substances examined were diamond, native sulphur, cryolite, rock-salt, sylvine, ruby, anhydrite, celestine, barytes, anglesite, apatite, phosphorite, topaz, zircon, beryl, kunzite, calcite, glass, and bakelite, an artificial amber-like material used for electric insulation. The view that the colours are due to dissociation of minute traces of impurities and the luminescence to the recombination of the products of dissociation is favoured. F. S.

Dependence on Temperature of the Dielectric Constant of some Gases and Vapours. Mario Jona (*Physikal Zeitsch.*, 1919, **20**, 14—21).—The dielectric constant of air, carbon dioxide, ammonia, sulphur dioxide, methyl alcohol vapour, and steam has been measured at a series of temperatures from 17·8° to 178·1°. Curves of the variation of the constant with temperature are given, and the significance of the curves is discussed mathematically.

J. F. S.

Significance of the Volta Effect in Measurements of Electromotive Equilibria. A. Smits and J. M. Bijvoet (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 562—569).—Application of the more recent views of electromotive equilibria to the Volta effect leads to the result that, on polarisation and passivation, the change in this effect must be great, and that in these phenomena the Volta effect would constitute even the greatest part of the total change in the electromotive force. It is found, further, that if the Volta effect between metals in which the state of internal equilibrium prevails are really very small, as is rendered probable by recent experimental work, this must be regarded as a characteristic property for metals in internal equilibrium.

The values found on measurement of potential differences for metal–electrolyte, termed experimental electrical potentials, always contain an unknown Volta effect, and it is this which renders impossible calculation from the said potentials of the saturation concentrations of the metal ions.

Relations have been derived which contain the solubility product of the metal, the solubility quotient of the non-metal, or the electron concentration in the electrolyte, but not the Volta effect, and these permit of the preparation of a solubility product series of metals and a solubility quotient series of non-metals, from which conclusions may be drawn as to the chemical and electrochemical behaviour of the metals. T. H. P.

Hydrogen Overvoltage. Duncan A. MacInnes and Leon Adler (*J. Amer. Chem. Soc.*, 1919, **41**, 194—207).—None of the theories advanced to account for overvoltage, with the exception of that of Möller (A., 1909, ii, 114), attempts to explain the great influence exerted by the physical condition of the electrode on the overvoltage, a polished platinum electrode, for instance, showing an overvoltage as high as 0·1 volt, whereas that for platinised platinum is nearly zero. The authors have made a number of measurements of hydrogen overvoltage with platinised platinum electrodes, use being made of an apparatus resembling, but differing in detail from, that of Thiel and Breuning (*Zeitsch. anorg. Chem.*, 1913, **83**, 329). With such low currents that one bubble of hydrogen appears in one or more minutes, fluctuations in the overvoltage are observed, the curve connecting overvoltage with time being sinuous with a sharp break invariably following the highest voltage. At low current densities, the bubbles come off at one point and continue to do so, no matter how long the observations are continued, so that each bubble probably leaves a nucleus behind it when it becomes detached.

In explanation of these results, it is assumed that molecular hydrogen, when formed from hydrogen ions by the reaction $2H^+ + 2\epsilon = H_2$, goes directly into solution in the electrolyte immediately surrounding the electrode, so that the hydrogen at that point will tend to rise in concentration and produce a supersaturated solution unless carried away by diffusion, stirring, or other means. If,

however, a nucleus of gaseous hydrogen is present in the electrode, a portion of the hydrogen will enter this gaseous phase, either directly from the electrode or by absorption from the electrolyte, the gaseous nucleus thus playing a part similar to that of a small crystal in a supersaturated salt solution. Hydrogen gas in the form of small bubbles must have a higher energy content per mol. of gas than the same volume of undispersed gas, as energy must be expended in overcoming the surface tension in the formation of small bubbles. Such bubbles will be more soluble, that is, will remain in equilibrium with more concentrated dissolved hydrogen, than the undispersed gas, this phenomenon being analogous to the increase in solubility produced by the fine grinding of solids. Since, other factors being constant, the potential at a hydrogen electrode depends primarily on the concentration of the dissolved hydrogen, an electrode in equilibrium with the small bubbles will reach a higher potential than a similar electrode in equilibrium with the undispersed gas. As electrolysis proceeds and the nucleus of gaseous hydrogen grows, the energy necessary to produce further growth must decrease, since the value of the ratio, increase in surface : increase in volume, is continually decreasing; if the bubble grows slowly, the hydrogen-bearing solution surrounding the electrode will tend to get into equilibrium with the bubble. This accounts for the decrease in overvoltage from a maximum point of the sinuous curve to a minimum point, where the buoyant effect of the solution is sufficient to overcome the attraction of the electrode for the bubble, which breaks away, leaving a nucleus behind. On the rising part of the curve, the concentration of the dissolved hydrogen is increasing to a value such that the nucleus can again grow, and so on. As the bubbles are not always evolved at the minimum points of the curve, it seems probable that, since the nuclei tend to form in depressions in the electrode, the bubbles that separate from the nuclei remain in these depressions until forced out by the growth of succeeding bubbles.

If the electrode can adsorb large hydrogen gas nuclei to start bubble formation, the supersaturation cannot rise to high values and the electrode will have a low overvoltage; metals with small adsorptive powers, however, hold small nuclei and have high overvoltages.

Support of the above explanation is furnished by microscopic examination of various electrodes when evolving hydrogen, this indicating experimental agreement with a theoretical quantitative relation between the size of the bubbles from, and the overvoltage of, platinised platinum electrodes. Further, theory indicates that the overvoltage should increase as the pressure decreases, and this is shown to be the case by the authors' results and also by unpublished work of H. M. Goodwin and L. A. Wilson. T. H. P.

The Modality of Reactions and Chemical Dynamics; Application to the Phenomena of Electrolysis and Spectroscopy. J. MEUNIER (*Bull. Soc. chim.*, 1919, [iv], **25**, 49—68).—The

chemical dynamics are the same, in principle, in the different forms of electric cells, which only differ amongst themselves in their complex and variable, secondary reactions. There is the same analogy in the production of spectral rays. The appearance of rays in the spectrum does not characterise, as is usually stated, an element, but rather a reaction of this element, and consequently indicates the presence of another element reacting with it. W. G.

Theory of Specific Heat. II. Walter Jankowsky (*Zeitsch. Elektrochem.*, 1919, **25**, 1—3. Compare A., 1918, ii, 59).—The author answers the criticism of Drucker (A., 1918, ii, 216) made in connexion with the earlier paper, and a further development of the theory of specific heat is contributed. It is shown that the statement that the change of the specific heat with temperature disproves the law of Dulong, Petit, and Joule is incorrect, for in every case regular relationships exist between the specific heat, the number of atoms, and the molecular weight. J. F. S.

Specific Heat Determinations at Higher Temperatures. Walter P. White (*Amer. J. Sci.*, 1919, [iv], **47**, 44—59).—In determining the specific heats of various substances at temperatures up to 1400° by the method of mixtures, the errors in the final result frequently approach one part per thousand even with precise work. The chief sources of error are: (1) the determination of temperature in the furnace, (2) the loss of heat during the dropping of the charge, (3) the exposure of the calorimeter to the atmosphere during the drop, (4) the effect of external conditions on the calorimeter, and (5) internal effects, such as auxiliary changes in the interior of the calorimeter after the drop.

Of these errors, the variability of the heat losses attending the dropping of the hot substance into the water is surprisingly great and should be prevented.

Modifications in furnaces and in methods of transference to the calorimeter are described in detail. [See, further, *J. Soc. Chem. Ind.*, 1919, 158A.] A. B. S.

Specific Heats of Silicates. II. Walter P. White (*Amer. J. Sci.*, 1919, [iv], **47**, 1—43. Compare A., 1909, ii, 966).—The specific heats of various silicates at various temperature intervals from 0—1400° were determined, using the method of mixtures, with greater precision than hitherto.

For quartz and silica glass, the values of the interval specific heats satisfy the expressions:

Quartz	$0{\cdot}1685+0{\cdot}000194\theta-0{\cdot}00000011\theta^2$
Silica glass.....	$0{\cdot}1670+0{\cdot}000189\theta-0{\cdot}000000125\theta^2$

The "instantaneous," or true atomic heats, rise regularly from about 3·5 at 0° to about 5·96 (with anorthite to 6·6) at 1300°, the value given by the classical kinetic theory.

The variations of the atomic heat from the theoretical constant

are due partly to secondary thermal effects connected with expansion, change of state or chemical action, and partly to the universal tendency towards a maximum value at a high temperature. The location of the development curve agrees approximately with the values of the atomic vibration frequency, calculated from the known properties of the atoms.

The difference in the value of the elements and compounds shows that it is not a property of the atom, but appears to be related to the combined oxygen.

The calculated specific heat of silica glass at constant volume and that at constant pressure are equal, but the actual heat–temperature curve of silica glass above 600° is above the theoretical value; that of the cristobalite is identical with the theoretical curve at 900°, but then rises above it. With albite and microcline, the specific heat at constant pressure is considerably above the specific heat at constant volume, and this confirms the evidence that the theoretical value of the dimension constant A in the expression $C_p - C_v = [A(3a)^2\Theta]/Kd$ is exceeded at high temperatures.

On comparing the specific heats of various silicates in the crystalline and glassy form, respectively, it was found that the specific heat of the glass is seldom greater than that of the crystal.

A. Smits' attempts to correlate inversion with equilibrium–temperature changes in liquids or liquid and solid systems have been examined with negative results, and it is suggested that premature fusion due to impurities and sluggishness of transformation account for the observed phenomena.

The conclusion is drawn, from the expansion and specific heats of solids being much less anomalous and irregular than those of liquids, that the molecular changes in solids are of a different order of magnitude. The author partly agrees with Bridgman that there is no relation between the volume, specific heat, and cohesion of pre-inverted and inverted substances, but considers that the change of properties during inversion, although rapidly accelerated at times, is nowhere sudden and discontinuous.

The observed difference in the atomic heat of different crystalline forms of the same substance is so irregular that similar differences with substances of unlike composition must be interpreted cautiously. [See, further, *J. Soc. Chem. Ind.*, 1919, 140A.]

A. B. S.

Specific Heat of Aqueous Solutions with Special Reference to Sodium and Potassium Chlorides. W. R. Bousfield and C. Elspeth Bousfield (*Phil. Trans.*, 1919, [*A*], **218**, 119—156).—The specific heat of aqueous solutions of sodium chloride and potassium chloride of various concentrations has been determined by the same method and using the apparatus previously described (A., 1911, ii, 580). In each case, the mean specific heat over the temperature ranges 0—13°, 13—26°, and 26—39° was determined. The results of the present work indicate that the specific heat and

specific volume of the combined water may be treated as approximately constant, and the lowering of the specific heat and specific volume of the free water on the introduction of a solute are each proportional to the percentage concentration of the solute. In dilute solutions, the specific heat curve approximates to that of water, which has a minimum at about 25°. In concentrated solutions, the variation of the specific heat with temperature appears to follow an almost straight line law. This behaviour is attributed to the simplification of the water by a considerable destruction of ice and steam molecules, and is analogous to the corresponding phenomenon noted previously (Bousfield and Lowry, A., 1905, ii, 135). The relationship $(dQ/d\theta)_H = L(d\chi/dH)_Q$ is found between the heat of dilution and the contraction. The following constants have been derived: (i) for potassium chloride: the specific heat of the liquid solute, 1·655; the molecular heat of the liquid solute, 123·4; (ii) for sodium chloride: specific heat of the liquid solute, 2·433, and the molecular heat of the liquid solute, 142·1. The number of molecules of water combined with a molecule of solute is calculated for various dilutions. J. F. S.

Neumann-Kopp's Law. Friedrich Bürki (*Helv. Chim. Acta*, 1919, **2**, 27—38).—For a number of the elements, the difference, $C_p - C_v$, between the atomic heats at constant pressure and at constant volume has been calculated by means of the formula $C_p - C_v = Ta^2V/41{\cdot}89x$ cal., where V is the atomic volume, a the coefficient of cubical expansion, and x the coefficient of compressibility; for chemically related elements, the differences are, as a first approximation, the same.

In the case of the haloids of the elements of the first group of the periodic table, the Neumann-Kopp law is more exactly fulfilled for molecular heats at constant pressure than for molecular heats at constant volume. C. S.

Determination of Melting Points by means of Electric Heating. Siegfried Laurens Malowan (*Zeitsch. angew. Chem.*, 1919, **32**, i, 16).—Two test-tubes are fastened concentrically one inside the other, leaving a small air-space at the sides and 15 mm. between the bottoms of the tubes. The inner tube is provided with a two-holed rubber stopper, one hole for the thermometer, the other for slipping in the melting-point tube. For making a melting-point determination, the apparatus is fixed with the bottom of the outer tube 5 mm. inside the mouth of a small electrically heated Heraeus crucible furnace. It is claimed that the temperature control is better and the results more accurate than with the usual forms of melting-point apparatus, and, in addition, the whole apparatus can be very quickly cooled. E. H. R.

Boundaries of Existence of the Liquid State. G. Bruni (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 394—397).—The author criticises the conclusions drawn by Herz (A., 1918, ii, 150), who, like Meyer (A., 1918, ii, 292), has overlooked the fact that the true

melting point (triple point, solid–liquid–vapour) does not delimit the liquid state at its lower boundary, the melting point varying with the pressure. Herz considered only twenty-two out of eighty-eight elements, and his deductions have neither theoretical bearing nor empirical confirmation. T. H. P.

Application to Eight Different Substances of the Formula which Expresses the Heat of Vaporisation of a Liquid. E. Ariès (*Compt. rend.*, 1919, **168**, 444—447).—Using the formula previously given (compare *ibid.*, 204), the author has calculated the heat of vaporisation for carbon dioxide, ammonia, stannic chloride, methyl formate, pentane, hexane, heptane, and octane, and finds that the calculated results agree very well with those obtained by different workers. W. G.

Limits of Separation by Fractional Distillation: A New Still-head. S. F. Dufton (*J. Soc. Chem. Ind.*, 1919, **38**, 45—46T). —The still-head described consists of an open tube inside which is another, closed, one with a wire wound spirally round it so that it just fits the outer tube. The latter may be made of parts of different sections increasing in diameter downwards, this gradation of the annulus serving to carry away the increasing volume of condensed liquid; a form more easily constructed consists of one length of tubing of approximately uniform bore, the spirals being wound on cores of decreasing diameter. For any particular set of conditions, there is a certain minimal value for the working volume of the still-head; if this is exceeded, there is no consequent increase in the amount of inseparable mixture in the still-head, the extra length at the bottom becoming filled with vapour and liquid of one of the pure constituents. Such still-heads are far more efficient than the Young pear-bulb column in common use, and have the great practical advantage that the distillation, having been started at the proper rate, slows down and stops when the limit of each pure constituent is reached, rise in the temperature being then necessary to drive off the next constituent. From a mixture of 5 c.c. of benzene with 10 c.c. of toluene, 4·6 c.c. of benzene and 9·4 c.c. of toluene were recovered by direct distillation; the loss was 0·3 c.c. and the unseparated intermediate portion 0·7 c.c., which is not far removed from the actual working volume, the total volume found in the flask at the end of the operation being just twice this amount.

A similar arrangement provides a very efficient means of washing a gas with a small quantity of liquid. In this case, the annulus is made of the same size throughout, and the pitch of the wire spiral is kept as small as practicable so as to reduce the speed of descent of the liquid. Such a washer gives more intimate average contact between gas and liquid and introduces no hydrostatic pressure. T. H. P.

Ultramicroscopic Examination of very thin Deposits, of Metals and Salts, obtained by Evaporation in High Vacua. L. Hamburger (*Kolloid Zeitsch.*, 1918, **23**, 177—199).—The thin

deposits produced on the walls of a vessel in which metals and other substances have been strongly heated have been examined by means of an ultramicroscope. The metals were mounted in the form of thin wires and heated electrically in a vacuum; salts, such as sodium chloride and calcium fluoride, were heated on a tungsten wire. It was found that on admitting air to the cooled vessel, changes in the nature of the film occurred, and in consequence the film was protected by a thin layer of Canada balsam before air was admitted and the ultramicroscopic examination made. The experiments were carried out with the metals silver, gold, tungsten, molybdenum, platinum, iron, copper, nickel, magnesium, zinc, and cadmium, and also with carbon, sodium chloride, and calcium fluoride. It is shown that the metals with high melting points, molybdenum, platinum, nickel, and iron, and also carbon, produce sublimates which are either completely unresolvable or mainly unresolvable into particles. The lower melting elements with a higher vapour tension, gold, silver, copper, magnesium, zinc, and cadmium, show a greater tendency to a less disperse condensation and produce a complete network of ultramicrons. Generally, it can be stated that the higher the temperature necessary for slow sublimation the finer is the structure of the sublimate. The electrical conductivity of films of gold, silver, platinum, and tungsten of measured thickness has also been determined, and it is shown that a covering of calcium fluoride or Canada balsam is a very efficient protection for these metals. Films condensed at the temperature of liquid air, on warming to the ordinary temperature, undergo a non-reversible change of resistance, which is very great in the case of gold and silver. This is probably due to a change in the structure of the deposit, for ultramicroscopically the deposits are seen to be different at the two temperatures. Many deposits undergo a change of resistance when there is no temperature change. In particular, silver deposits produced and kept at the ordinary temperature for long periods increase in their resistance to an infinitely large value. This must be due to changes in the optically unresolvable part of the deposit which lies between the network. These changes are probably of such a nature that small gaps occur, and consequently the direct metallic contact is broken. The influence of the temperature of the walls on which the deposit is formed has been investigated, and it is shown that the higher the vapour tension of the metal is at the temperature of the walls, the less disperse is the structure of the deposit. Many of the metals produce films of definite colours which are characteristic of the metal and are determined by the selective absorption of light by the atoms. J. F. S.

Evaporation and Condensation Velocities and the Calculation of Chemical Constants from the Density of the Condensate. Max Trautz (*Zeitsch. anorg. Chem.*, 1919, **105**, 97—111).—A mathematical discussion of the equilibrium between vapour and liquid treated as a simple chemical reaction. From the

gas theory and the thermodynamic laws, formulæ are developed expressing evaporation and condensation velocities in terms of heat of evaporation, molecular heat, molecular weight, molecular diameter, density of the condensate, and closeness of packing. The chemical constant of the "reaction" is the logarithm of the ratio of the maximum evaporation and condensation velocities. It increases with increasing molecular diameter, with decreasing molecular volume, and with decreasing density of packing of the molecules. With increasing molecular weight the constant first rises and subsequently falls continuously. It is shown that all the factors involved in the calculation of the evaporation and condensation velocities can be given a purely mechanical interpretation, with the exception of the heat of evaporation. For the first time a purely mechanical interpretation of the chemical constant is given, its calculation requiring only the molecular diameter, molecular weight, and density.

The method of investigation here used, involving a mathematical analysis of the processes occurring at the surface between two phases, is applicable to other problems, such as the solution of gases in liquids and diffusion problems. E. H. R.

The Extension of the Gas Laws to Liquids and Solids. JOHN SCOTT HALDANE (*Biochem. J.*, 1918, **12**, 464—498).—The three gas laws may be combined and more correctly stated, and at the same time extended to liquids, in the form: The intermolecular volume of a given volume of gas or liquid varies inversely as its mean intermolecular pressure, and directly as the absolute temperature, the concentration of gram-molecules, and a constant which is the same for all gases and liquids. This may be embodied in the equation $P(V-v)=22{\cdot}4nT/273$ or $P(V-v)=0{\cdot}082nT$, where P = mean intermolecular pressure in atmospheres, V = volume in litres, v = volume virtually occupied by the molecules themselves, n = relative number of molecules, so that when P and $n=1$ and $T=273°$ absol., $P(V-v)=22{\cdot}4$. This casts new light on the physical properties of solutions and on various phenomena connected with gases and liquids. Thus it can be shown that: (*a*) Diffusion pressure of any one substance between one liquid or gas and another is proportional to the values of its partial pressures p in the one liquid or gas, and $1-v$ in the other. (*b*) The intermolecular pressure is the same for all solutions in the same solvent, up to high concentrations and with wide variations of temperature. (*c*) Osmotic pressure is simply the increased intermolecular pressure required to neutralise the excess of diffusion pressure of a pure solvent inwards over that of a diluted solvent outwards, through a membrane permeable to the solvent, but not to the solute which dilutes it. This excess is given by the equation

$$p_0=0{\cdot}082NT(n/N_1-n),$$

where p_0 = osmotic pressure and n, N, N_1 = gram-mols. of solute, pure solvent, and solution per litre. (*d*) Diminution of vapour pressure of the solvent and rise of vapour pressure of the solute are propor-

tional to n/N_1. (*e*) Elevation of b. p., and depression of m. p., of the solvent are proportional to $n/(N_1-n)$, and can be calculated respectively if the latent heats of boiling or melting of solvent are known. (*f*) When the ratio n/N_1 is the same in different solutions with the same solvent, the substances, of which n denotes gram-mols. per litre (including the solvent), are in diffusion equilibrium, and their mutual diffusion pressure is $0{\cdot}082NT(n/N_1)$. This diffusion pressure, which has, hitherto, often been confused with osmotic pressure, is of fundamental importance in physical chemistry and physiology. W. G.

The Dissociation Pressures of some Nitrides. Roland Edgar Slade and Geoffrey Isherwood Higson (T., 1919, **115**, 215—216).

Structure of Crystals in very thin Laminæ. New Experimental Determination of Molecular Dimensions. René Marcelin (*Ann. Physique*, 1918, [ix], **10**, 189—194).—The method employed in the investigation consists in examining a thin sheet of the substance between crossed nicols side by side with a thin wedge of quartz which is moved until the same colour is obtained with both, and from the indices of refraction of the quartz and the thickness of the wedge at the measured point calculating the thickness of the lamina of substance under investigation. By this method laminæ of mica and *p*-toluidine have been examined, and it is shown that with mica laminæ may be obtained of thickness equal to the diameter of the molecules. With *p*-toluidine laminæ have been obtained which are certainly not thicker than twice the molecular diameter and probably not thicker than a single molecular diameter. J. F. S.

The Theory of Gels. Samuel Clement Bradford (*Biochem. J.*, 1918, **12**, 351—381. Compare A., 1917, ii, 366).—The low diffusion constant of the natural emulsoids, by retarding the crystallisation of the hot sols, allows the accumulation of a large excess concentration, which, together with their large value of K in von Weimarn's formula, causes gelation on cooling. The small crystallisation velocity is also responsible for the permanency of the gels and the hysteresis of the sols. The viscosity changes in the sols of the natural emulsoids, by heating, are seen to be in conformity with Einstein's formula, since thermal changes cause alterations in the numbers, as well as the size, of the crystallisation centres. Applying von Weimarn's theory to the reversible sol-gel transformation, the conclusion is drawn that gels should comprise two phases, namely, an ultramicroscopic solid phase, bathed in a liquid dispersion medium, from which it has crystallised and which it retains partly by molecular and partly by capillary forces.

Complex organic substances and such as are highly aggregated in solution tend to crystallise as spherites, and this leads to the supposition that the ultimate solid particles of gels are spherites. This

is supported by the fact that by suitable precipitation with alcohol gelatin can be made to assume the form of microscopic spheres.

The liquid adsorbed at the liquid–solid boundary surfaces of gels is under an internal pressure intermediate between those of the solid and of the liquid. This intermediate value of the internal pressure is much greater than that of the free liquid and conditions certain peculiarities in the properties of gels. W. G.

Velocity of Coagulation. H. R. Kruyt and A. E. van Arkel (*Chem. Weekblad*, 1919, **16**, 220—225).—A preliminary note on the measurement of the velocity of coagulation of colloidal solutions. The hydrosol studied is that of selenium prepared by the reduction of selenious acid by means of hydrazine. The concentration of the hydrosol was determined by direct enumeration of the particles under the ultramicroscope, the progress of the coagulation being exhibited by the fall in concentration observed from time to time over a period of thirteen days after the addition of the electrolyte. In presence of potassium chloride solutions of concentration 10 and 20 mg. mol. per litre coagulation of the standard sol was scarcely perceptible; with 40 and 50 mg. per litre coagulation was extremely rapid. The concentration 30 mg. per litre brought about coagulation at a convenient measurable rate. W. S. M.

Forms assumed by Drops and Vortices of a Gelatinising Liquid in Various Coagulating Solutions. Emil Hatschek (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 303—316).—The effect of allowing a 14% gelatin sol to fall drop by drop into a solution of aluminium sulphate or ferrous sulphate is described, and illustrations of the forms assumed by the gelatin drops are given in the paper. Temperature and the density of the coagulating medium determine to a large extent the form assumed. By dropping a solution containing 10 grams of gelatin and 8 grams of crystallised potassium ferrocyanide into a solution of copper sulphate of suitable density, discs were produced which bear a remarkable resemblance to highly magnified blood corpuscles. The effect of the addition of a large number of substances to the gelatin solution is also described. J. F. S.

Investigations dealing with the State of Aggregation. IV. The Flocculation of Colloids with Salts containing Univalent Organic Ions. S. B. Schryver and Nita E. Speer (*Proc. Roy. Soc.*, 1919, [*B*], **90**, 400—414).—If adsorption of the discharging ion plays the chief part in the flocculation of colloids, it might be expected that those salts the normal solutions of which have the lowest surface tension would exhibit the greatest flocculating capacity. This capacity was investigated for a series of sodium salts of organic acids and of hydrochlorides of organic bases, of which the normal solutions show wide variations in the surface tensions. As a general rule no relationship was shown to exist between surface tension of the solutions and flocculation capacity.

In only one case, that of the mastic sol, did such a relationship exist—the hydrochlorides of those bases the solution of which had lower surface tensions precipitating the mastic in lower concentrations. It is suggested by the authors that two classes of suspensoid should exist, namely, those which owe their charge to an ion derived from a salt from which they are obtained by hydrolysis, as, for example, the chlorine ion in the ferric hydroxide sol obtained by dialysis of ferric chloride solutions, and those which owe their charge to an ion derived by dissociation in a colloid acting as an electrolyte in which the active, rapidly moving ion is held electrostatically in an outer layer to the other more slowly moving colloidal ion. The former class are designated exionic and the latter endionic colloids. Mastic belongs probably to the latter class. S. B. S.

Equilibria in the Reduction of Oxides by Carbon. Roland Edgar Slade and Geoffrey Isherwood Higson (T., 1919, **115**, 205—214).

Relations between Distribution Ratio, Temperature, and Concentration in System: Water, Ethyl Ether, Succinic Acid. George Shannon Forbes and Albert Sprague Coolidge (*J. Amer. Chem. Soc.*, 1919, **41**, 150—167).—The published data on the solubilities and distribution ratios for this system being insufficiently numerous and concordant, a complete set of new determinations has been made. The ethyl ether used was carefully purified, especially from alcohol, a trace of which may be detected by means of the green coloration given with strong sodium hydroxide solution containing a little permanganate; the presence of 1% of ethyl alcohol is found to increase the solubility of ether in water by about 2%, and that of succinic acid in ether by about 20%, the effect on the solubility of the acid in water being much less. The method of analysis used consisted in shaking a mixture of the desired composition in a "pyrex" vessel shaped like a submarine with periscope; as the stopper is in contact with neither the contents of the vessel nor the water of the thermostat, it need not be greased, danger of contamination being thus obviated. The vessel was rocked at such a speed that the air bubble travelled the whole length to and fro, the rocking being stopped for ten minutes and the two layers extracted separately by inclining the vessel first one way and then the other. Special pipettes were used, which did not require greased stoppers and which allowed of the evaporation of the solutions without transference to other vessels.

The compositions of solutions unsaturated with one of the constituents were determined at 15°, 20°, and 25°, and a series of measurements of the distribution ratio was made at each of the three temperatures and at various concentrations of acid.

If s is the mol. fraction of succinic acid (undissociated) in the water layer, and e, w, σ, ω, and ϵ those of ether in the water layer, water in the water layer, succinic acid in the ether layer, water in the ether layer, and ether in the ether layer, respectively, the com-

plete differential of the distribution ratio ($R=s/\sigma$) with respect to temperature is shown to have the form $dR/dt=(b+an)/\sigma(1-am)-s(\beta+\alpha\nu)/\sigma^2(1-\alpha\mu)$, where $\alpha=[\delta\sigma/\delta\omega]_t$, $\beta=[\delta\sigma/dt]_\omega$, $\mu=[\delta\omega/\delta\sigma]_t$, and $\nu=[\delta\omega/\delta t]_\sigma$. The reasoning involved is followed out by means of a solid diagram. Further, an expression is derived for the value of dR/dt between solutions having constant composition of solvent (compare Herz and Kurzer, A., 1910, ii, 399, 1045), the value thus obtained for dR/dt being 0·0257, whereas the expression given above yields the result, $dR/dt=0·0258$.

Succinic acid is not distributed in constant ratio between water and ether; the ratio of activity to concentration in aqueous solution falls with increasing concentration, or, more strictly, this deviation is greater in water than in ether solution, solvation being undoubtedly largely responsible for this phenomenon.

Application of Rothmund and Wilsmore's mutual solubility equation (A., 1902, ii, 447; compare Nernst, A., 1901, ii, 647) to the solubility data at 20° shows that 60 mols. of H_2O furnish 33 molecules of water, which therefore consist almost entirely of $(H_2O)_2$; this result is only an approximate one, but it agrees well with estimates made by other workers using different methods (compare Richards and Palitzsch, this vol., ii, 97). T. H. P.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XIV. Binary Solution Equilibria between Pyrogallol and the Aromatic Amines or Acid Amides. Robert Kremann and Ludwig Zechner (*Monatsh.*, 1918, **39**, 777—805. Compare A., 1918, ii, 69; this vol., ii, 54). —Previous results have led the authors to the conclusion that pyrogallol, as a trihydroxyphenol, should be capable of uniting with three molecules of a primary amine unless the close proximity of the hydroxy-groups leads to steric hindrance. The latter is found to be the case, since pyrogallol unites with only two molecules of aniline, *p*-toluidine or β-naphthylamine, and with but one molecule of α-naphthylamine; with the isomeric phenylenediamines, compounds of the type, 2 molecules pyrogallol + 2 molecules diamine, are obtained, whilst with the para-isomeride there is also formed a compound of two molecules of the phenol with one of the diamine. As is to be expected, an equimolecular compound of pyrogallol and benzamide is found to exist, and a similar compound is in all probability formed from acetamide. H. W.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XV. The Binary Systems of Benzophenone with Phenols and their Derivatives. Robert Kremann and Ludwig Zechner (*Monatsh.*, 1918, **39**, 807—832).—The affinity of different classes of substances towards phenols generally appears to be weakened by the replacement of the methyl by the phenyl group in the former; the work now described was undertaken with the object of obtaining a direct comparison of acetone and benzophenone in this respect.

Benzophenone forms equimolecular compounds with phenol and α-naphthol, thus resembling acetone; with β-naphthol, the three mononitrophenols, the three dihydroxybenzenes, and pyrogallol, on the other hand, it gives simple eutectics. It therefore appears that the ability of a phenol to form compounds with benzophenone is lessened by the introduction into it of groups which strengthen its electronegative character. H. W.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XVI. The Binary Systems of Benzophenone and certain Amines. Robert Kremann and Rudolf Schadinger (*Monatsh.*, 1918, **39**, 833—838).—The inability of benzophenone to yield compounds with negatively substituted phenols (preceding abstract) might be due merely to steric hindrance or to insufficient difference in the heteropolarity of the components, such that whilst the electronegative carbonyl group can react with amphoteric phenol, it is unable to do so with its electronegative derivatives. In the latter case, it appeared probable that benzophenone would react with amines. Experiment, however, shows that it yields simple eutectics with *p*-toluidine and with α- or β-naphthylamine. The difference in behaviour of benzophenone towards phenol on the one hand and towards negatively substituted phenols on the other must be ascribed to steric hindrance. H. W.

Velocity of Reaction in the System $2NO + O_2$. Max Trautz (*Zeitsch. Elektrochem.*, 1919, **25**, 4—9).—Polemical between the author and Bodenstein on the method adopted in calculating from the experimental results in connexion with the above-named system (see Bodenstein, A., 1918, ii, 302; Trautz and Dalal, A., 1918, ii, 162). J. F. S.

Relationship of the Constants of Formation and Hydrolysis of Esters of Symmetrical Dicarboxylic Acids. Anton Skrabal (*Monatsh.*, 1918, **39**, 741—763).—A theoretical consideration of the subject and partial review of the literature. The author is led to the following conclusions.

The esterification of a symmetrical dicarboxylic acid and the hydrolysis of its normal ester in the presence of acid lead to an "acid-ester" equilibrium (2 acid ester $\rightleftharpoons$ normal ester + dicarboxylic acid), the constant, K, of which is related to the constant ratios of consecutive hydrolysis and esterification in accordance with the equation $nn' = K$. If, therefore, the acid-ester equilibrium is not appreciably altered by change in temperature and other experimental conditions, nn' must be constant. This is most readily the case when both n and n' are of the order unity, and when, further, $n = n'$. Actually, K is found to be practically independent of the temperature, and its numerical value is frequently 4, hence the simplified constant ratio, $n = n' = 2$. The acid-ester equilibrium is displaced with decreasing acidity, and in consequence the relation-

ship of the constants for alkaline hydrolysis differs from that for acidic hydrolysis.

The esterification of a symmetrical dihydric alcohol and the hydrolysis of its normal ester leads to an "ester-alcohol" equilibrium (2 ester alcohol $\rightleftharpoons$ normal ester + alcohol), the constant, K, of which is related to the constant ratios of the consecutive actions according to the equation $nn'=K$. The "ester-alcohol" equilibrium is not influenced by the acidity, and the relationship of the constants is consequently the same for acid and alkaline hydrolysis.

Replacement of the alkyl group is analogous to esterification and hydrolysis. Consecutive replacement in a symmetrical mixed ester leads to the establishment of a "mixed-ester" equilibrium, the constants of which are similarly related to the ratios of the constants for consecutive replacement. The ratios of the constants of the hydrolysis and formation of mixed esters are governed by their relationships to the constants of the two acid-ester equilibria (or ester-alcohol equilibria) and of the mixed ester equilibrium.

The dynamic conception of the ester equilibrium imposes necessary, but not complete, conditions with respect to the relationship of the constants of formation and hydrolysis of symmetrical diesters and its variation with the experimental conditions. The possible variations are limited by the simultaneous application of the parameter rule (A., 1916, ii, 607). The latter leads to assumptions which can be experimentally tested, and are therefore valuable working hypotheses. H. W.

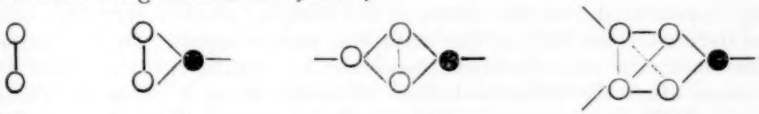
Consecutive Reactions. V. Dynamics of the Oxalic Ester Equilibrium. ANTON SKRABAL and DANICA MRAZEK (*Monatsh.*, 1918, **39**, 697—739. Compare A., 1916, ii, 477; 1917, ii, 250; 1918, ii, 12).—The hydrolysis of normal methyl oxalate, the esterification of oxalic acid, and the reaction of the acid ester in aqueous-alcoholic solution have been kinetically investigated at 25°. The acid titre and the amount of normal ester have been analytically determined at given intervals of time. All three processes show uniformly that the relationship of the constants is 2:1 both for the consecutive hydrolysis of the normal ester and for the consecutive esterification of oxalic acid. The esterification equilibrium of oxalic acid has been determined for both stages of the process. H. W.

Hydrolysis of Ethyl Oxalate with Alkali. ANTON SKRABAL and ANTON MATIEVIC (*Monatsh.*, 1918, **39**, 765—773).—To gain insight into the influence of the nature of the alkyl group on the velocity of hydrolysis of esters, the authors have examined the behaviour of ethyl oxalate under conditions similar to those used with the methyl ester (A., 1917, ii, 250). Comparison of the constants obtained with those found for the methyl ester shows the latter to undergo the first stage of hydrolysis three times as rapidly, and the second stage two and a-half times as rapidly, as the ethyl ester. H. W.

Studies in Catalysis. X. The Applicability of the Radiation Hypothesis to Heterogeneous Reactions. WILLIAM CUDMORE MCCULLAGH LEWIS (T., 1919, **115**, 182—193).

Chemical Structure of Atoms. I. FRANZ WENZEL (*J. pr. Chem.*, 1918, [ii], **98**, 155—203).—A theoretical paper containing the following sections:

I. *Typical Elements.*—The author's method of building structural forms of atoms is based on two hypotheses. The first is that the tervalent nitrogen atom is composed of two nuclei united by a double linking (compare A., 1918, ii, 17); in addition to the three valencies, four others are involved in the double linking, thus —●=●<. The second hypothesis is that the mass 14·01 of the nitrogen atom is distributed uniformly over these seven valencies, so that with each valency corresponds a mass of approximately two units, designated valency mass 2. It is assumed, therefore, that to each valency is related a definite mass magnitude. This is usually 2, but in connexion with the atoms of lithium, glucinum, and boron a valency mass 3 must be assumed. Starting, therefore, from the helium atom (composed of two singly linked nuclei) the elements of the first small period can be built up by the systematic addition to both nuclei of the helium atom of valency masses 2 and 3 in numbers increasing from 1 to 7; thus,



He. Li. Gl. B.

(○ = valency mass 2; ● = valency mass 3.)

carbon, nitrogen, oxygen, and fluorine are represented by similar structures containing 6, 7, 8, and 9 valency masses respectively. Analogous structures can be formed for the elements of the second period, starting from the neon atom. The author claims that these structures, which are not at variance with the physical properties of atoms, are fitted to express the most important chemical properties of the elements and render possible the treatment of general questions, such as variability of valency and the cause of the metallic and metalloid characteristics of elements.

II. *Valency Masses and their Mode of Linking.*—Assuming that the forces which hold together the valency masses in the atomic nucleus can be treated as valency forces, the maximal value of the valency masses 2 and 3 (and also of valency mass 1, from which valency masses 2 and 3 must be assumed to be derived) can be ascertained. By introducing these maximal values of the valency masses into the structural pictures above, structural formulæ are obtained which allow the deduction of many interesting phenomena, such as (*a*) the existence of a metallic form of the quinquevalent nitrogen atom, on which are founded the ammonium compounds, (*b*) the variations of the atomic weights from whole numbers, (*c*) a

structural formula of the hydrogen atom which appears to account for its metallic properties and for the variation of its atomic weight from exactly 1.

III. *Stereoisomerism of Ammonium Compounds.*—The preceding theory of atomic structure leads to the evolution of a model of the nitrogen atom which is in agreement with crystallographic requirements concerning the spatial positions of the atoms in ammonium iodide and in tetramethylammonium iodide. By the help of this model the possibilities of isomerism to be anticipated in ammonium compounds can be derived. These are exceedingly complicated, and of all the nitrogen models hitherto proposed only the pyramidal formula of Bischoff is applicable for the graphic representation of the isomerism of ammonium compounds, and then only if it is amplified by the insertion of a diagonal in the square base. For the explanation of such isomerism chemistry must call in the help of crystallography in a much greater degree than has hitherto been the case. The isomerism of the optically active ammonium compounds requires for its establishment the conception of a binuclear nitrogen atom.

IV. *The Metallic Carbon Atom.*—It is known that one of the valencies of the carbon atom occasionally functions with basic properties (Baeyer's carbonium valency). This necessitates a "metallic" carbon atom, the structure of which includes the grouping characteristic of the atoms of the metals. Such a structure can be derived from that of the metalloid carbon atom. In the latter the valencies are directed tetrahedrally, whilst in the metallic carbon atom the three metalloid valencies lie in a plane to which the metallic valency lies at right angles, a spacial disposition of the valencies of the metallic carbon atom which the author claims is confirmed by the position of the atoms in the crystal lattice of graphite. C. S.

New Reflux Condenser. James J. Bajda (*J. Ind. Eng. Chem.*, 1919, **11**, 52).—A side-tube, leading from the stem of the condenser just above the flask containing the volatile liquid, conducts the vapours into the top of the condenser jacket, where they enter the condensing coil. The lower part of the latter is formed into a siphon-trap, which delivers the condensed liquid into the flask through a tube extending down the stem of the condenser. A branch tube on the coil just above the trap extends through the top of the condenser jacket. W. P. S.

An Efficient Laboratory Funnel for Filtering Neutral Liquids, especially the Volatile Organic Solvents. T. B. Aldrich (*J. Ind. Eng. Chem.*, 1919, **11**, 139—140).—In this funnel the filter paper is clamped securely between two plates, so that it cannot lift even when the suction is interrupted; the formation of channels and passages for the liquid and precipitate beneath is thus avoided. The funnel is of aluminium and consists of four parts: (1) a cast hollow cylinder with a small flange at the top and a

heavier one at the bottom, both outside, the lower one being screwed; (2) a plate 1·5 mm. thick perforated with 0·75 mm. holes (3 mm. centre to centre); (3) a ring, threaded on the inside and milled on the outside; (4) a conical lower portion provided with a stem and having a flange at the top threaded on the outside to mesh with the threads on the inside of the ring. After the filter-paper has been introduced the ring is screwed up and holds the other three parts together, rubber rings being inserted to render the joints tight. T. H. P.

Inorganic Chemistry.

Chemical Reactions at Low Pressures. IV. The Clean-up [complete removal] of Nitrogen by a Heated Molybdenum Filament. Irving Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 167—194. Compare A., 1915, ii, 467).—When molybdenum filaments are heated at 2000—2400° K in nitrogen at pressures of 40 bars or less (0·03 mm.), great care being taken to exclude moisture, the filaments lose weight at the same rate as if heated in a vacuum. The nitrogen does not attack the filaments, but disappears at a rate independent of the pressure if the latter exceeds 1 bar; the amount of the nitrogen thus disappearing is much less than the chemical equivalent of the molybdenum evaporated, and the ratio, ϵ, of the number of molecules of nitrogen removed to the number of atoms of molybdenum evaporated in the same time decreases from a maximum of about 0·4 to a minimum of about 0·01 as the temperature of the filament or bulb is raised.

With very minute pressures of water-vapour such as result even in presence of drying agents from failure to "bake out" the bulb, no complete removal of nitrogen occurs, although under such conditions molybdenum will remove carbon monoxide and tungsten will remove either nitrogen or carbon monoxide, the value of ϵ in each of these cases being unity.

The fact that ϵ is independent of the pressure, but dependent on the filament and bulb temperatures, indicates that the reaction occurs in the space around the filament, and that each collision between molybdenum atoms and nitrogen molecules results in combination, at least two products being formed; these are probably a first order compound of the formula NMoN and a second order compound, $Mo{:}N_2$, the proportion between the amounts of these two depending on the relative velocity of the molecules at the moment of collision and on the internal velocity of the nitrogen molecules. The former compound is very stable and cannot be decomposed on the bulb by heating to 360°, its formation being favoured by low relative translational velocity of the colliding molecules and by high

internal or rotational velocity in the nitrogen molecule. All those collisions which do not yield the first order compound give that of the second order, which is so unstable that it decomposes practically completely on striking the bulb, owing to the attractive forces between pairs of molybdenum atoms being much greater than between these and nitrogen molecules.

The deposit which collects on the bulb has the following properties. It is spongy and can easily be rubbed off with the finger on opening the bulb, whereas deposits formed in a high vacuum are dense and can scarcely be scratched off with a knife. If the bulb is kept at the temperature of liquid air, the deposit formed gives up some nitrogen when warmed to the ordinary temperature, but only part of this nitrogen is absorbed again on cooling the bulb; the larger part of the nitrogen in the deposit is not, however, liberated by heating in a vacuum at 360°. The deposit very rapidly absorbs up to about one-thirtieth of its chemical equivalent of nitrogen when cooled by liquid air, but it does not readily absorb hydrogen under these conditions. At the ordinary temperature or above, however, large quantities of hydrogen are absorbed or dissolved by the deposit, these being given up slowly at 300° in a good vacuum. When heated in nitrogen at 270° or above, the deposit combines with nitrogen, and this is not given off again at 360° in a vacuum. The deposit reacts rapidly with water-vapour at the ordinary temperature with production of hydrogen, much of which remains dissolved in the deposit until liberated by heating. T. H. P.

Formation of Ammonia by the Electric Discharge. E. Briner and A. Baerfuss (*Helv. Chim. Acta*, 1919, **2**, 95—100).—As the result of experiments on the production of ammonia from nitrogen and hydrogen by means of the electric arc it is found that the yield of ammonia is more than doubled when the ratio of nitrogen to hydrogen is increased from 1:3 to 15:3 by volume. This result, which appears to contradict the rule that the optimum mixture for the formation of a substance corresponds with the composition of that substance, is explained on the ground that at the temperature employed the active participants in the reaction are the atoms, not the molecules, of the two gases and that an excess of nitrogen will be necessary if this gas is more difficultly activated than hydrogen. [See also *J. Soc. Chem. Ind.*, 1919, April.] C. S.

Combustion of Ammonia in a Deficiency of Oxygen. F. Raschig (*Zeitsch. physikal. Chem. Unterr.*, 1918, **31**, 138—142; from *Chem. Zentr.*, 1918, ii, 1016—1017).—It is generally considered that the combustion of ammonia in an excess of oxygen results in the formation of nitric oxide and water; the author considers this view to be erroneous, or, at any rate, not proved. When oxygen is in deficit, reaction is commonly supposed to proceed according to the equation (i) $4NH_3+3O_2=2N_2+6H_2O$. Müller (*Zeitsch. physikal. Chem. Unterr.*, 1913, 169) has, however, shown

that under these conditions a quantity of gas is formed containing about 59% nitrogen and 41% hydrogen, and has assumed that a portion of the ammonia dissociates into its constituent elements at the high temperature of the flame. If this were actually the case, considerable quantities of nitrogen should be formed when oxygen is in excess, whereas the yield of nitric acid is actually 90% and over. An explanation may be found in the formation of the hypothetical di-imide when oxygen is in deficit: [(ii) $NH_3+O_2=N_2H_2+2H_2O$], which would probably decompose into nitrogen and hydrogen. The author has heated potassium hydrazinesulphonate with potassium hydroxide in the expectation that the hydroxyhydrazine primarily formed would immediately pass into di-imide by loss of water; actually, the calculated amount of potassium sulphite was formed and a mixture of equal volumes of nitrogen and hydrogen was evolved. A similar result was obtained by the decomposition of benzenesulphonhydrazide, $NH_2{\cdot}NH{\cdot}SO_2Ph$. Müller's experiments can be interpreted by supposing that the combustion of ammonia takes place partly according to equation (i) and partly with formation of di-imide. It is, however, possible that the first reaction does not occur at all, but that combustion proceeds with intermediate formation of hydrazine [(iii) $4NH_3+O_2=2N_2H_4+2H_2O$], which subsequently decomposes into nitrogen and hydrogen. Actually, the author has been able to establish the production of hydrazine (by isolation of benzylazine) when oxygen burns in ammonia. Combustion, therefore, probably proceeds mainly in accordance with equation (ii), and to a less extent according to equation (iii), whilst oxidation in accordance with equation (i) may be considered not to occur at all. H. W.

Formation of Azoimide by Oxidation of Hydrazine. A. Angeli (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 389—393).—The author's experiments (A., 1894, ii, 93) were carried out in accordance with theoretical considerations which referred to the analogies in behaviour shown by hydrazine, hydroxylamine, and hydrogen peroxide, and were completely confirmed experimentally. Browne and Overman (A., 1916, ii, 245) and Sommer (A., 1917, ii, 30), on the other hand, attempted merely to obtain an explanation of a reaction discovered accidentally by them, namely, the formation of azoimide by oxidation of hydrazine, the only connection with the author's work lying in the fact that, to explain the formation of azoimide from hydrazine some intermediate poly-nitrogenated compound must be assumed. This intermediate term is probably tetrazone, $NH_2{\cdot}N{:}N{\cdot}NH_2$ (A., 1917, i, 452; compare Willstätter and Pfannenstiehl, A., 1905, i, 723). T. H. P.

The Oxidation of Nitric Oxide by Dry Air. André Sanfourche (*Compt. rend.*, 1919, **168**, 307—310. Compare this vol., ii, 105).—A study of the oxidation of nitric oxide by dry air at temperatures ranging from −50° to 525°. The first stage in the oxidation, namely, the conversion of nitric oxide into nitrogen

trioxide, is practically instantaneous and independent of the temperature between the limits given. The next stage, the oxidation of the nitrogen trioxide to nitrogen peroxide, is regulated by the reversible reaction, $2N_2O_3+O_2 \rightleftharpoons 4NO_2$, in which the displacement is from left to right up to 200°, but tends more and more towards right to left as the temperature rises from 200° to 525°. W. G.

The Cycle of Oxidation of Nitric Oxide in the Presence of Water. André Sanfourche (*Compt. rend.*, 1919, **168**, 401—404).—In the presence of water, nitric oxide is oxidised to nitrogen trioxide and not to the peroxide, the trioxide then being decomposed by the water, giving nitric acid and a partial regeneration of nitric oxide. In the presence of nitric acid (D 1·5), however, the nitrogen trioxide is oxidised with the formation of the peroxide and water, according to the equation $2HNO_3+N_2O_3=H_2O+2N_2O_4$. This oxidation is first noticeable with nitric acid (D 1·3), which has a concentration of approximately 50%, but is not complete, and progresses further as the concentration of the nitric acid used is increased. W. G.

Apparatus [to Demonstrate] the Decomposition of Nitric Acid at a Red Heat. H. Böttger (*Zeitsch. physikal. Chem. Unterr.*, 1918, **31**, 152; from *Chem. Zentr.*, 1918, ii, 1005).—The apparatus consists of a small quartz distilling flask provided with a dropping funnel and connected with an inclined condenser and small glass cylinder; the stopper of the latter carries a glass tube leading to a pneumatic trough for the collection of oxygen. Condenser and cylinder are cooled by a freezing mixture. The nitric acid is allowed to drop into the strongly heated flask; a green liquid, consisting of condensed nitrogen peroxide, water, and unchanged nitric acid, collects in the cylinder. H. W.

Electrochemical Preparation of Salts of Perphosphoric Acid and of Monoperphosphoric Acid. Fr. Fichter and Antonio Rius y Mirò (*Helv. Chim. Acta*, 1919, **2**, 3—26. Compare Fichter and Müller, A., 1918, ii, 439; Rius y Mirò, this vol., ii, 63).—Most of the work has been already published (*loc. cit.*). The amount of monoperphosphoric acid increases with increasing current density, with decreasing total concentration, and with decreasing alkalinity. If the electrolysis is prolonged to produce high concentrations, the current yield decreases largely. With suitable electrodes, the yield of perphosphate is 64% and of monoperphosphate somewhat more than 7%. These salts are formed in moderate yield even in the absence of fluoride provided the electrolyte is rich in alkali; also both peroxidised salts are obtained by the electrolysis of a mixture of tetrapotassium and dipotassium pyrophosphates. In strongly acid solution, perphosphoric acid decomposes spontaneously in about two days into monoperphosphoric acid and phosphoric acid. Monoperphosphoric acid also decomposes in acid solution, but much more slowly than in alkaline solution. C. S.

Graphitic Carbon. V. Kohlschütter (*Zeitsch. anorg. Chem.*, 1919, **105**, 35—68).—The physical and chemical properties of graphite vary within such wide limits that no distinct line of demarcation can be drawn between graphite on the one hand and amorphous carbon or soot on the other. From the consideration of a mass of data relating to the properties and mode of occurrence of natural graphite, and the methods of formation and properties of artificial graphite and amorphous carbon, the author comes to the conclusion that all varieties of graphite and amorphous carbon are different physical forms of "black carbon," which is to be regarded as an allotropic modification of diamond. The properties of different samples of graphite depend on the conditions under which it is produced, and its variable character is to be attributed to different degrees of dispersity. The reactions favourable to the production of graphite fall into three groups: (1) surface reactions; (2) reactions *in situ*; (3) surface layer reactions. These are all reactions of the localised type which have been grouped together in a previous paper in the class of "topochemical" reactions (this vol., ii, 156). As an example of the first group, the decomposition of acetylene by copper at 400—500° produces graphite as the result of a slow surface reaction, whereas the spontaneous decomposition at a higher temperature in unlimited space produces soot. The formation of graphite by the decomposition of a carbide, as in the Acheson process, is an example of the second group, and another example is the precipitation of graphite from iron–carbon solutions, where in all probability crystals of cementite are first formed, which then decompose, leaving the graphite particles as pseudomorphs of the cementite crystals. As examples of the third group, there are those reversible reactions which lead to graphite formation, such as the decomposition of carbon disulphide. In these cases, temperature is of importance only in so far as it determines the rate at which equilibrium is attained. Contrary to the generally accepted view, temperature and pressure have little influence on graphite formation except in so far as they influence other conditions.

It is probable that all natural graphite has been formed by a localised reaction of one of the above types. It may in some cases have been formed by metamorphosis of organic carbon in contact with igneous rock, more often probably by the decomposition of carbon monoxide in clefts, catalysed by the metallic oxides present.

The view that there is no essential difference between graphite and amorphous carbon is borne out by the work of Debye and Scherrer on the constitution of graphite and amorphous carbon (A., 1917, ii, 437), which showed that both have the same interference effect on X-rays. The conclusion of these authors that in graphite the carbon atoms are arranged hexagonally in plane layers which are superimposed on one another is in agreement with the present author's idea that graphite owes its peculiar properties to its lamellar structure. This type of structure not only accounts for its peculiar physical properties, but also for many chemical

properties, such as its resistance to oxidation and to reagents, and for the fact that its formation is favoured when free carbon is produced by a surface reaction. The difference between the densities and heats of combustion of graphite and amorphous carbon is discussed, and is shown not to be detrimental to the theory that they are essentially the same form of carbon. The formation of graphitic acid by oxidation of graphite and not of amorphous carbon is due to the peculiar structure of the former and not to the existence of a distinct graphite molecule. E. H. R.

Graphitic Carbon and Graphitic Acid. V. Kohlschütter and P. Haenni (*Zeitsch. anorg. Chem.*, 1919, **105**, 121—144).—For the further elucidation of the structure of graphite (preceding abstract), the oxidation of graphite to graphitic acid and the properties of the latter have been studied. Since the properties of the graphitic acid depend on those of the graphite used, in order to obtain results which could be reproduced, the experiments were confined to a specially pure electrically prepared graphite free from ash. The oxidations were carried out with a mixture of potassium chlorate, nitric and sulphuric acids in the cold under fixed conditions. The peculiar oxidising properties of this mixture are due to the fact that it penetrates the whole mass of the graphite; other oxidising agents which do not penetrate the graphite have little action or oxidise it completely to carbon dioxide.

Repeated treatment of the graphitic acid with the oxidising mixture changes its colour from green to brown or yellow, whilst its carbon content gradually diminishes. Thus after one treatment, the graphitic acid has the composition C = 59·02%, H = 1·91%, O = 39·07%, and after five oxidations, C = 54·4%, H = 2·14%, O = 43·46%. The apparently crystalline particles of graphitic acid are not crystals, but pseudomorphs of the original graphite particles. After repeated washing with water, the graphitic acid passes into solution. The colloidal solution can be flocculated by dilute acids, and the precipitated gel is perfectly soluble in water. The differently coloured graphitic acids merely differ in their degree of dispersity, the more lightly coloured products, obtained by repeated oxidation, being more highly disperse. It is not true, as was formerly supposed, that the colour of the graphitic acid depends on the sample of graphite from which it is made.

When heated or treated with reducing agents, graphitic acid is reduced to carbon. Heating experiments have shown that the gases evolved are water, carbon monoxide, and carbon dioxide, the ratio CO/CO_2 being greater the more slowly the heat is applied. The temperature at which the decomposition becomes explosive is also lower the slower the heating, and if the heating is very slow the decomposition may go quietly to completion without explosion. The black, voluminous residue consists of carbon (99·7% C). It has all the properties of soot, but can be compressed into a mass very similar to graphite. When the decomposition of the graphitic

acid by heat takes place under pressure, the graphitic character of the residual carbon is more marked. By decomposing the graphitic acid under sulphuric acid at 160—180°, a residue was obtained having properties intermediate between those of soot and graphite. Treatment of graphitic acid with reducing agents, such as ferrous or stannous salts, gave products with strongly marked graphitic properties, giving graphitic acid again when oxidised. These products, however, were contaminated with adsorbed iron or tin compounds, which were difficult to remove.

The results of these experiments are held to confirm the opinion expressed in the former paper (*loc. cit.*) that graphite is formed when the reaction resulting in the formation of free carbon is spatially confined (topochemical reaction), and that the difference between graphite and amorphous carbon is purely physical, depending on the conditions of formation. The formation of graphitic acid is likewise topochemical in character, the graphitic acid retaining the structure of the original graphite. E. H. R.

Course of Reaction in Explosions of Dilute Carbon Disulphide-Air Mixtures. G. R. Stewart and John S. Burd (*J. Ind. Eng. Chem.*, 1919, **11**, 130—133).—In the combustion of dilute mixtures of carbon disulphide and air, containing from 2·5 to 4% of the former, from 40 to 60% of the carbon disulphide is oxidised according to the equation $CS_2+3O_2=CO_2+2SO_2$; from 25 to 35% follows the reaction $2CS_2+5O_2=2CO+4SO_2$; the remainder, 15 to 30%, is unchanged. Sulphur trioxide does not seem to be formed. With a mixture containing 2·5% of carbon disulphide, the resulting gases contain about 15% of oxygen, 1% of carbon dioxide, usually less than 1% of carbon disulphide and carbon monoxide, and about 4% of sulphur dioxide. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Precipitated Amorphous Silica. P. Braesco (*Compt. rend.*, 1919, **168**, 343—345).—From a study of the dilatation of precipitated silica, cast into sticks by admixture with 5% of sodium silicate as a paste and subsequently dried and calcined, the author finds that precipitated silica is amorphous provided that it is only heated to about 600°, but that, if it is calcined at a temperature exceeding 1000° it is crystalline and of the same form as cristobalite. W. G.

Nature of the Gas Evolved when Fused Sodium Hydroxide is Dissolved in Water. W. H. Schramm (*Chem. Zeit.*, 1919, **43**, 69—70).—Evolution of gas is sometimes noticed when fused sodium hydroxide is dissolved in water; the greater part of this gas is air contained in the sodium hydroxide, but a small quantity of oxygen, in addition, is also present. For example, 400 grams of fused sodium hydroxide, when dissolved in water free from dissolved gases, yielded 14·45 c.c. of gas containing 28·7% of oxygen. The quantity of oxygen in excess of that due to the air is derived

from the decomposition of an alkali compound of a higher ferric oxide; this compound is present in the sodium hydroxide, and is probably sodium perferrite, $Na_2O{\cdot}Fe_2O_4$. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Normal and Acid Sulphates of Sodium. Paul Pascal and Ero (*Bull. Soc. chim.*, 1919, [iv], **25**, 35—49).—A study of the equilibrium of the ternary mixture, Na_2SO_4–H_2SO_4–H_2O, over a temperature range from $-30°$ to 120°. The results confirm the existence of the following anhydrous salts and hydrates: Na_2SO_4 and its hepta- and deca-hydrates; $Na_2SO_4,NaHSO_4$; $NaHSO_4$; $NaHSO_4,H_2O$; $NaHSO_4,H_2SO_4$; $NaHSO_4,H_2SO_4,1{\cdot}5H_2O$; $2NaHSO_4,Na_2SO_4$.

There was no indication of the formation of the hydrate of the intermediate salt, $Na_2SO_4,NaHSO_4$, or of the hydrate, $Na_2SO_4,2{\cdot}5—3H_2O$.

Determinations were also made of the temperatures of commencement of solidification of solutions of sodium sulphate in different concentrations of sulphuric acid. Anhydrous normal sodium sulphate is only obtained at the higher temperatures and from dilute acid. From results obtained with solutions of sodium hydrogen sulphate it is shown that, in order to crystallise this sulphate, a considerable quantity of acid must be added to the solution, an acidity equal to 65% sulphuric acid being necessary in order to obtain the anhydrous hydrogen sulphate, the acid sulphates of the type $NaHSO_4,H_2SO_4$ only being obtained with an acidity exceeding 80%.

In order to recover some of the acid from sodium hydrogen sulphate, one of two processes may be adopted. At the ordinary temperature a 40—45% solution of the acid sulphate may be prepared and then cooled to $-20°$, the liquid being sown with a crystal of the decahydrate, $Na_2SO_4,10H_2O$. The liquid separates into a solid phase, and a liquid phase containing at the most 30% of sulphuric acid and about 10% Na_2SO_4. The second method suggested is to prepare a 75% solution of the anhydrous hydrogen sulphate at 100° and cool to the ordinary temperature. The liquid phase obtained contains about 50% of sulphuric acid. [See *J. Soc. Chem. Ind.*, 1919, April.] W. G.

Basic Exchange in Silicates. II. E. Ramann and A. Spengel (*Zeitsch. anorg. Chem.*, 1919, **105**, 81—96).—Experiments have been made on the action of mixed salt solutions on ammonium permutite, prepared by treating sodium permutite with ammonium nitrate. With mixed solutions of potassium and calcium chlorides in equivalent concentrations, the ammonium is completely replaced. The composition of the resulting permutite is independent of the total salt concentration between 0·1 and 3·25*N*. The ratio of the bases in the end-product is generally different from their ratio in the solution, the final permutite containing relatively more of that base of which there is a smaller proportion in the solution. When potassium, ammonium, and, in most cases, sodium are the predomin-

ating bases in the solution, the base ratio in the final permutite corresponds with the ion ratio in the solution. When, however, calcium predominates in the solution, the proportion of calcium in the permutite is much smaller than would correspond with its ion proportion in the solution. Calcium chloride solutions do not bring about complete basic exchange with either ammonium, potassium, or sodium permutite. It is concluded that basic exchange in the case of such silicates as permutite is an ion reaction following the general mass action law, but in the case of calcium, and to some extent sodium salts, a disturbing factor, probably of a physical character, comes into play (compare A., 1917, ii, 468).

E. H. R.

Silver Amalgams Rich in Silver. N. Parravano and P. Jovanovich (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 411—412; *Gazzetta*, 1919, **49**, i, 6—9).—Silver amalgams rich in silver were prepared similarly to the gold amalgams (see this vol., ii, 161). The specific electrical conductivity curve is not continuous, but consists of two distinct branches: the first extends from 0 to about 2% of mercury, and has the form characteristic of solid solutions. The second, from about 2% to 14% of mercury (the highest proportion of mercury attainable by the method of preparation used), is a straight line, this being characteristic of alloys composed of two distinct crystalline individuals; the latter are the saturated mixed crystals with 2% of mercury and, according to Reinders (A., 1906, ii, 219), the compound, Ag_3Hg.

T. H. P.

[Pure] Calcium Hypochlorite to Replace Dakin's Solution. P. Michaelis (*Münch. med. Woch.*, 1919, **66**, 45).—The Griesheim-Electron works manufacture as "hyporit" an almost pure calcium hypochlorite containing a little calcium chloride and very little lime; it has over 80% of available chlorine, and forms a stable powder which can be compressed into tablets of accurate dosage. It readily dissolves in water to an almost clear, very faintly alkaline solution, which replaces that of Dakin.

G. B.

Yellow Cuprous Oxide. L. Moser (*Zeitsch. anorg. Chem.*, 1919, **105**, 112—120).—The best method for preparing yellow cuprous oxide is by the reduction of a cupric salt by means of hydroxylamine in presence of alkali. It can also be prepared electrolytically, using an alkali sulphate as the electrolyte and an anode of pure copper. When a copper salt is reduced by Fehling's solution the character of the precipitated cuprous oxide depends on the relative proportion of tartrate solution used; when excess of tartrate is used, red, crystalline cuprous oxide is formed, but with little tartrate, the cuprous oxide is yellow and amorphous.

As first precipitated the amorphous cuprous oxide is light yellow in colour and is probably a hydroxide. In absence of air the colour quickly changes to orange or brick-red, probably through loss of water. It can then be dried without further change. The dried

product contains a variable quantity, 2—3%, of water, held probably by adsorption. At high temperatures, above a low red heat, the water is lost and the yellow, amorphous oxide changes into the red, crystalline form. The yellow cuprous oxide is to be regarded as a primary metastable form, the red, crystalline form being the stable one. E. H. R.

The Carburation of Ceric Oxide. A. Damiens (*Ann. Chim.*, 1918, [ix], **10**, 330—352. Compare A., 1918, ii, 442).—The author shows that the product described by Sterba (compare A., 1902, ii, 399) as an oxycarbide of cerium, $CeC_2,2CeO_2$, is not a definite compound at all. The formation of cerium carbide, CeC_2, in an electric furnace takes place in three stages: $2CeO_2+C=Ce_2O_3+CO$, $Ce_2O_3+9C=2CeC_3+3CO$, $CeC_3=CeC_2+C$. The carbide, CeC_3, is soluble in the cerous oxide, and the intermediate products obtained in the carburation are really solid solutions of this nature, their content of the carbide, CeC_3, varying with the intensity of carburation. This higher carbide in its turn decomposes, giving the known carbide, CeC_2, and graphite, thus accounting for the fact that a pure carbide has never been obtained. W. G.

Disperse Aluminium Hydroxide. I. V. Kohlschütter (*Zeitsch. anorg. Chem.*, 1919, **105**, 1—25).—The physical form of any solid substance appearing as the result of a chemical reaction is influenced by the many variable factors which collectively determine the conditions operative at the time of its formation. In particular is this the case when the sphere within which the reaction can take place is limited or localised, as where a solid is formed by a reaction between a second solid and a liquid or gas, the reaction being localised at the surface of the solid. The author's work on the different forms of silver and arsenic (A., 1913, ii, 589, 953) demonstrated the dependence of the physical form of the product on that of the starting material. It is suggested that such strictly localised processes as those here cited should be termed "topochemical" reactions. The study of such reactions is important in connexion with the chemical and physiological processes in plants and animals, and for the study of mineral morphology.

As a noteworthy example of a topochemical reaction, the author has studied the formation of pseudomorphs of aluminium hydroxide by the action of ammonia solution on crystals of aluminium sulphate or ammonium alum. When crystals of either of these salts are immersed in ammonia solutions (1—10*N*), more or less perfect pseudomorphs of the original crystals in aluminium hydroxide are formed, the change being quite rapid and complete. The pseudomorphs can be dried, and sometimes even ignited, without losing their form. The physical characteristics of the pseudomorphs vary very considerably with the reaction conditions, depending especially on the ammonia concentration, temperature, nature of the original crystals, and the nature of the salts present in the reacting solution. For the experiments, crystal particles of graduated sizes were used,

and in order to characterise the resulting pseudomorphs, the average size of the particles was measured after drying at 40°, 110°, and at dehydrating temperature. The pseudomorphs were always smaller than the original crystals, the shrinkage being greater when stronger ammonia solutions were used. The density of the pseudomorphs was always greater from alum than from aluminium sulphate, other conditions being the same. The presence of other salts in the reacting liquor, such as ammonium sulphate, chloride, nitrate, and carbonate, had a considerable influence on the character of the product. The denser pseudomorphs were generally more transparent than the lighter ones.

The pseudomorphs are undoubtedly true gels. After drying at 40° they are rapidly peptised by dilute hydrochloric acid, but after drying at 110° peptisation is slower. The character of the sol obtained varies with that of the pseudomorphs in the same way as their density. The peptisation experiments indicate that the degree of dispersity is greatest in the densest pseudomorphs. The mechanism of the formation of the pseudomorphs and of their peptisation is discussed, the latter being considered a chemical reaction between the hydroxide and acid, as suggested in a previous paper (A., 1916, ii, 485). E. H. R.

The Behaviour of some Alkali Alumino-silicates at High Temperatures. H. Leitmeier (*Zeitsch. anorg. Chem.*, 1919, **105**, 69—80).—The work here described was undertaken to ascertain whether alkali–aluminosilicates, by heating for some time at a temperature just below their melting point, undergo decomposition with loss of alkali to such an extent that the accuracy of the melting-point determination would be affected. Two minerals were examined, a very pure form of orthoclase, adularia, m. p. 1145±5°, and the sodium aluminosilicate, labradorite, m. p. 1245—1250°. Samples of each mineral were kept upwards of 500 hours at a temperature 10° below the melting point. A small and gradually increasing loss of weight was always observed, of the order of about 0·2%. The loss of weight is attributed to loss of alkali, but is too small to confirm by direct alkali estimation. E. H. R.

Purification by Sublimation, and Analysis, of Gallium Chloride. Theodore W. Richards, W. M. Craig, and J. Sameshima (*J. Amer. Chem. Soc.*, 1919, **41**, 131—132).—The method here described for the purification of gallium salts is based on the fact that gallium trichloride sublimes and distils at a low temperature, whereas other chlorides likely to be associated therewith are much less volatile. In the apparatus used, gallium could be burnt in pure, dry chlorine, and the impure gallium trichloride thus obtained distilled in pure chlorine, in nitrogen, and in a vacuum successively; the parts of the apparatus were fused together, so that rubber connexions and ground joints were avoided. Distillation in nitrogen or in a vacuum was found necessary to eliminate dissolved chlorine. The resulting product showed no trace of any other substance in its

spark spectrum when examined in a Hilger wave-length spectrometer. In the best of three preliminary experiments, 0·43947 gram of gallium chloride yielded 1·07087 gram of silver chloride, having required 0·80587 gram of silver for complete precipitation; the values of the atomic weight of gallium calculated from these two data are 70·09 and 70·11 respectively; the determination is to be repeated with larger quantities of the gallium chloride.

T. H. P.

Purification of Gallium by Electrolysis, and the Compressibility and Density of Gallium. Theodore W. Richards and Sylvester Boyer (*J. Amer. Chem. Soc.*, 1919, **41**, 133—134).—The separation of gallium from indium by a method based on the different solubilities of the hydroxides of the two metals in alkali hydroxide solution is incomplete, the gallium thus obtained always containing several per cent. of indium and never showing a higher melting point than 26·9°. Electrolysis in slightly acid solution of a salt of the gallium partly purified by the above process (compare Dennis and Bridgman, A., 1918, ii, 456) yields far better results, the melting point of the gallium deposited being 30·8°, which is higher than any value yet given in the literature.

The compressibility of solid gallium is found to be $2·09 \times 10^{-6}$, this value falling exactly on the curve representing compressibility as a periodic function of the atomic weight; gallium containing several per cent. of indium, as obtained by the hydroxide process, gives an appreciably lower value. For liquid gallium, the compressibility is $3·97 \times 10^{-6}$, a value almost exactly identical with that of mercury and nearly twice as great as that of solid gallium, although its specific volume is less. This result is in agreement with the universal law that solids have compressibilities distinctly less than those of the same substances as liquids, quite irrespective of their specific volumes.

The densities of solid and liquid gallium are 5·885 and 6·081 respectively.

T. H. P.

Influence of Different Factors on the Critical Velocity of Tempering of Carbon Steels. A. Portevin (*Compt. rend.*, 1919, **168**, 346—348. Compare A., 1917, ii, 372).—From a study of the time of tempering as a function of the diameter of homothetic cylinders, and of the hardness as a function either of the time of cooling or of the diameter of the cylinders, it is shown that, for a carbon-steel containing C = 1·07%, Mn = 0·08%, the ratio τ, time of cooling, to the diameter is given graphically by two straight lines, differing according as the diameter is above 14 mm. or below 13 mm., and at the same time the hardness undergoes a change of about 200 Brinell units. These two phenomena are the consequence of the sudden lowering of the temperature of transformation with cooling and of the change in the microstructure. The critical velocity of tempering, or, more exactly, the region of velocities of cooling in which this sudden change of phenomena occurs, appears to be the most characteristic property of steel in so

far as its tempering is concerned. The critical velocity is also influenced, notably by the manganese content of the steel, decreasing with it. The minimum temperature of hard tempering is a function of the velocity of cooling, and is lower as the velocity is higher.

Chevenard's results, using a steel wire 0·32 mm. in diameter (A., 1917, ii, 414), when compared with the author's results on a cylinder 20 mm. in diameter, made of steel of almost the same carbon and manganese content, lend support to the view that pressure plays an important part in the formation of troostite. W. G.

Some Mixed Crystals of Calcium Ferrite and Aluminate. Edward D. Campbell (*J. Ind. Eng. Chem.*, 1919, **11**, 116—120. Compare *ibid.*, 1913, **5**, 627; 1915, **7**, 835; A., 1914, ii, 772).—Cooling curve and micrographic investigations have been carried out in order to ascertain (1) if a calcium ferrite of the composition $5CaO,3Fe_2O_3$ really exists (compare Shepherd, Rankin, and Wright, A., 1911, ii, 725; Rankin and Wright, A., 1915, ii, 50; Sosman and Merwin, A., 1916, ii, 618), and (2) what is formed when a mixture of calcium oxide, ferric oxide, and alumina is melted and then cooled slowly enough to permit the material to be nearly in equilibrium during the entire cooling period. The results obtained confirm the statement that dicalcium ferrite, $2CaO,Fe_2O_3$, and monocalcium ferrite, CaO,Fe_2O_3, are the only definite compounds of lime and ferric oxide. Pure tricalcium aluminate, $3CaO,Al_2O_3$, may be recovered by crystallisation from a solution of lime in the compound, $5CaO,3Al_2O_3$, as a solvent provided that the concentration of the lime at the beginning of the crystallisation is less than is required to form tricalcium aluminate with all the alumina present. If a solution with the empirical formula $8CaO,3R_2O_3$, containing ferric oxide and alumina in the molecular proportion 1:3, is slowly cooled, mixed crystals with the ferric oxide and alumina in the ratio 1:7 crystallise out until the ratio $Fe_2O_3:Al_2O_3$ in the solution has been increased to 3:5; mixed crystals in the latter ratio then crystallise out, further increase in the $Fe_2O_3:Al_2O_3$ ratio being produced until, at about 1370°, the ratio reaches the value 1:1. Those aluminates in which part of the alumina is replaced by ferric oxide are capable of holding in solution less calcium oxide than the pure aluminates. T. H. P.

A New Method of Determining the Allotropic Transformation of Nickel. Ernst Jänecke (*Zeitsch. angew. Chem.*, 1918, **31**, i, 229; *Zeitsch. Elektrochem.*, 1919, **25**, 9—17).—Allotropic changes in metals are accompanied by a change in the rate of expansion, which, however, is so small that it is difficult to detect. The following method allows the change to be observed over short as well as long intervals of time. A nickel cylinder, 45 cm. long, is inserted in a low-pressure press (3000 kilos.) used for textile and compressive strength tests, and heated by means of a resistance furnace. The variation in length produces a movement of the upper movable plate of the press, which can be registered; move-

ments as small as 0·007 mm. are indicated. The transformation temperature of nickel is 347—360°; the expansion graph consists of two straight lines, that above the transformation temperature being the more steeply inclined. W. R. S.

Molecular Compounds with High Co-ordination Numbers and with Atomic Groups as Co-ordination Centres. The Stereochemistry of Inorganic Boron, Silicon, and Phosphorus Compounds. PAUL PFEIFFER (*Zeitsch. anorg. Chem.*, 1919, **105**, 26—34).—The type of crystal structure which has been revealed by the study of crystals by means of X-rays can be explained chemically on the assumption that the crystal is a complex molecular compound of the co-ordinated type. It is necessary, however, to assume that not only atoms, but also groups of atoms, may function as co-ordination centres, and that co-ordination numbers as high as 8 or 12 are possible. The distribution of the co-ordinated groups around the central atom or group can be represented by reference to a cube. When the co-ordination number is 4, the co-ordinated groups occupy alternate corners of the cube (tetrahedral grouping); six similar groups occupy face centres (octahedral grouping); eight groups occupy all cube corners (cubic grouping), and twelve groups are situated at the centres of cube edges (cubo-octahedral grouping). The author proceeds to show that a number of known compounds may be represented as co-ordinated compounds with co-ordination numbers 8 or 12. Among the former are included compounds of the type $[Mg(OH_2)_8]Cl_2$, $[Mg(OH_2)_8]BiCl_5$, $[Al(OH_2)_8]_2(SO_4)_3$, $[Ca(NH_3)_8]Cl_2$, and the well-known series of double nitrates of the rare earths of the type $[M''(OH_2)_8]_3[M'''(NO_3)_6]_2$. A number of double fluorides, cyanides, and oxalates are also included.

The alloys of the type $NaZn_{12}$, KHg_{12} are typical molecular compounds of the 12-co-ordinated type, and should have the same crystalline structure as the metals copper, silver, and gold. The alums can also belong to this type, $[M'''(OH_2)_{12}](SO_4)_2M'$, and also a number of dodecahydrates of metallic salts. Specially interesting in this connexion are the phospho-, silico-, and boro-tungstates described by Rosenheim and Jänecke (A., 1918, ii, 77). The respective tungstic acids may be represented by the formulæ:

$$\left[(P\overset{O''}{O_5})(WO_3)_{12}\right]H_7. \quad \left[(Si\overset{O_2''}{O_4})(WO_3)_{12}\right]H_8. \quad \left[(B\overset{O_3''}{O_3})(WO_3)_{12}\right]H_9.$$

In these formulæ, the central atom (P,Si,B) has six co-ordinated oxygen atoms, and the group (RO_6) itself functions as a co-ordination centre with twelve co-ordinated (WO_3) groups. In the group (RO_6) it is necessary to distinguish two kinds of oxygen atoms in order to account for the number of ionised hydrogen atoms in the molecule. This distinction brings in the possibility of the existence of isomerides, since the groups $\left(Si\overset{O_2''}{O_4}\right)$ and $\left(B\overset{O_3''}{O_3}\right)$ when given an octahedral space configuration can have both *cis* and *trans* forms. These considerations are in perfect agreement with

the facts, for both silicotungstates and borotungstates of this type are known in two forms, whereas no isomerism has been observed in the case of the phosphotungstates. E. H. R.

Investigation by means of *X*-rays of the Crystal Structure of White and Grey Tin. A. J. Bijl and N. H. Kolkmeijer (*Proc. K. Akad. Amsterdam*, 1919, **21**, 494—500, 501—504).—From the photographs of white and grey tin previously obtained (this vol., ii, 108), the crystal structures of the two forms have been deduced. T. H. P.

Gold Amalgams Rich in Gold. N. Parravano and P. Jovanovich (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 364—368; *Gazzetta*, 1919, **49**, i, 1—6. Compare this vol., ii, 69, 155).—Previous investigations by various authors lead to the conclusion that in gold amalgams containing between about 90% and 100% of gold, mercury exists dissolved in the gold to form solid solutions. In order more clearly to define the nature of these gold amalgams rich in gold, the authors have measured the electrical resistances at 25° of pure gold and of a series of twenty-one of the amalgams containing from 0·4859% to 9·593% of mercury. These amalgams were prepared by coating gold wire about 0·5 mm. in diameter electrolytically with mercury, heating the wire at 200° for two to three hours, then coating again with mercury and heating, this procedure being continued until the resulting amalgam assumed the desired composition. The homogeneity in composition of the amalgamated wires was demonstrated by microscopic examination and also by analysis. The specific conductivities of the different amalgams are given in the forms of a table and a curve, the latter showing a continuous diminution in the conductivity of gold by increasing proportions of mercury. This behaviour is characteristic for solid solutions. T. H. P.

Action of Alkalis on Crucibles made of Alloys of Platinum or of Gold. Paul Nicolardot and Claude Chatelot (*Bull. Soc. chim.*, 1919, [iv], **25**, 4—9).—Platinum crucibles undergo marked corrosion when sodium hydroxide or potassium hydroxide is fused in them, and the crucibles are subsequently washed, first with water and then with dilute acid. New crucibles resist better than old crucibles, and the presence of iridium rather diminishes the resistance to corrosion. Potassium hydroxide is decidedly more corrosive than sodium hydroxide. In the case of crucibles of alloys of gold, those made from gold–palladium alloys were the most resistant to the fused alkali hydroxides, but even this alloy was very seriously attacked by sodium peroxide at the concentration necessary for the decomposition of minerals such as chromite. Barium oxide at 825° is much less corrosive than the alkali hydroxides. W. G.

Mineralogical Chemistry.

Volcanic Explosions. I. Explosive Eruptions and their Phases. Combustion of Hydrogen. VENTURINO SABATINI (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 360—364).—Water-vapour alone is capable of explaining the mechanical effects produced in volcanoes and the projections from the latter, and there is evidence indicating that water-vapour constitutes almost the whole of the gaseous products of volcanic smoke columns; the source of this vapour is not yet established. At the high temperatures prevailing in the depths of volcanoes, the water-vapour is easily decomposable by various elements, with liberation of hydrogen; actual dissociation of the water-vapour to any large extent is improbable owing to the high pressures existing.

The presence of water in the lava may be derived from water of infiltration meeting the very hot lava and being absorbed and decomposed by it, the hydrogen and any residual uncombined oxygen passing up into the crater and there meeting the atmospheric oxygen entering through the fissures, and thus giving rise to violent explosion. The law connecting pressure and temperature inside the laval mass is not known, but it is probable that the latter does not increase at the same rate as the former. At the high temperatures prevailing at great depths, the hydrogen remains gaseous, and at 2000° reaches its maximal density (co-volume).

Laboratory experiments show that the minerals formed at the highest temperatures are spinels, melting at 1900°, whilst iron chromate melts at 1850°, quartz at 1775°, and peridotes at 1730° or above; others generally melt below 1700°. Thus at 2000° or, under high pressures, at a considerably lower temperature lava cannot contain elements in the solid condition. T. H. P.

Volcanic Explosions. II. Calculations on the Combustion of Hydrogen. Comparison with Ordinary Explosives. VENTURINO SABATINI (*Atti R. Accad. Lincei*, 1918, [v], **27**, ii, 405—407. Compare preceding abstract).—The energy developed in the explosion of one-ninth of a kilogram of hydrogen, with a co-volume of 1240 litres, is considered, and it is shown that 800,000 kilogram-metres remain available for rupturing the cup of the crater, for enlarging the latter, and for projecting matter therefrom, a loss of one-third of the energy in heat effect and in secondary shocks being assumed. With glyceryl nitrate and explosive gelatin, the corresponding amounts of energy given per kilogram are 625,000 and 652,000 kilogram-metres respectively. T. H. P.

Mimetite, Thaumasite, and Wavellite. E. T. WHERRY (*Proc. U.S. Nat. Mus.*, 1918, **54**, 373—381).—Colourless, acicular crystals from the Tintic district, Utah, were thought to be penfield-

ite until it was observed that they had different optical constants ($\omega=2\cdot14$, $\epsilon=2\cdot13$). An analysis made on 6 mg. proves them to be mimetite: PbO 73·3, Cl 2·5, As_2O_5 [24·7]%.

Crystals of thaumasite are described from West Paterson, New Jersey. Although minute, these give the axial ratio $a:c=1:0\cdot931\pm0\cdot003$, and several new forms. Thaumasite is described chemically as "di-hydroxy-tricalcium carbono-silico-sulphate crystallising with $14H_2O$ in the hexagonal system."

Wavellite, as divergent groups of minute, acicular crystals in ferruginous sandstone from Hellertown, Pennsylvania, gives the new axial ratio $a:b:c=0\cdot564:1:0\cdot404$. Analysis by F. Wynkoop agrees with the formula $(Al[OH,F])_3(PO_4)_2+5H_2O$ of Groth, rather than with that of Dana:

Al_2O_3.	P_2O_5.	SiO_2.	F.	H_2O.	Total.	Sp. gr.
36·5	33·4	1·1	0·8+	28·6	100·1	2·325

L. J. S.

Connexion between the Optical Constants and Chemical Composition of the Scapolites. N. Sundius (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 1—12).—The following determinations support the statement of Borgström (A., 1915, ii, 836) that in the minerals of the scapolite group the refractive indices and the double refraction increase with the percentage of carbon dioxide present. I, small, yellow grains with pyroxene from Hesselkulla, Sweden. II, fine-grained, crystalline material with calcite, pyroxene, etc., from Waldviertel, Lower Austria. III, white, fine-grained with little muscovite and calcite, from Froland, Arendal, Norway. IV—VI, from Vahâive, Pahtosvaara, and Kalpivaara respectively, all in the Kiruna district, Swedish Lapland:

	Chloride-marialite.	Sulphate-marialite.	Carbonate-marialite.	Sulphate-meionite.	Carbonate-meionite.	ω	ϵ	$\omega-\epsilon$.
I.	3	—	27	—	70%	1·5880	1·5534	0·0346*
II.	4	—	36	—	60	1·583	1·549	0·035
III.	71	2	—	—	27	1·5516	1·5427	0·012
IV.	36	6	—	—	58	1·575	1·550	0·025
V.	71	—	—	6	23	1·554	1·541	0·0134
VI.	75·5	—	—	3	21·5	1·550	1·540	0·0101

* I, sodium-light; II—VI, daylight.

	SiO_2.	Al_2O_3.	CaO.	Na_2O.	Cl.	SO_3.	CO_2.	H_2O.	Total.	Sp.gr.
I.	45·53	28·41	17·49	n.d.	0·10	0·04	4·61	n.d.	96·18	2·730
II.	48·60	27·07	15·69	n.d.	0·17	0·02	4·48	0·23	96·26	2·710
III.	56·82	22·14	7·51	7·64	2·89	0·22	1·14	1·08	100·12*	—

* Incl. K_2O, 0·72.

L. J. S.

Composition of Tourmaline from Utö, Sweden. Hj. Sjögren (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 317—324).—The occurrence of tourmaline of different colours in the lithia-bearing pegmatite veins of the Island of Utö, near Stockholm, has long been known. Analyses by N. Sahlbom are of I, the pink variety ("rubellite"); II, pale green; III, greyish-white, nearly colourless; IV, bluish-black. The first three are alkali-tourmalines, and the last an iron-tourmaline. Details are given of the method of analysis. Some of the iron is perhaps present in the ferric state, especially in IV. The results agree closely with the general formula, $H_{20}B_2Si_4O_{21}$, of Penfield and Foote (A., 1899, ii, 304):

	SiO_2.	B_2O_3.	Al_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	Li_2O.	P_2O_5.
I.	36·70	10·76	42·99	1·35	0·28	0·60	0·10	0·49	3·36	0·89	nil.
II.	36·48	9·74	40·08	3·51	0·40	trace	0·08	0·86	2·99	1·11	0·17
III.	36·33	9·79	40·99	1·35	0·37	0·95	0·16	0·50	3·04	1·31	nil.
IV.	35·40	10·45	34·69	9·04	0·41	1·08	0·89	0·60	3·15	0·72	0·13

	F.	$H_2O<105°$.	$H_2O>105°$.	Total less O for F.
I.	0·19	0·24	2·75	100·62
II.	0·40	0·17	3·85	99·64
III.	0·39	0·45	4·02	99·46
IV.	0·29	0·09	2·64	99·46

L. J. S.

Analyses of Swedish Glauconites. Naima Sahlbom (*Bull. Geol. Inst. Univ. Upsala*, 1916, **15**, 211—212).—Analysis I is of material from coarsely crystalline Silurian limestone at Eriksöre, Öland. The glauconite was separated from the crushed rock by means of an electromagnet and pure grains picked out under a lens. The grains are olive-green and sharply angular with rough surfaces. Brown, weathered grains were rejected. The material is slowly decomposed by hot hydrochloric acid. At 100° it loses 1·60% H_2O. II is of material mixed with quartz grains from Schonen. The grains are irregularly rounded, with dull lustre and dark green colour; they more closely resemble the ordinary type of glauconite than I. The material is difficultly attacked by hot hydrochloric acid. It loses 2·7—3% H_2O at 100°:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.
I.	51·35	9·47	16·37	4·75	0·63	3·17	7·34
II.	52·74	12·29	9·35	6·30	0·55	4·05	7·97

	Na_2O.	F.	P_2O_5.	H_2O. > 100°.	Total.	Sp. gr.
I.	1·22	—	0·35	4·85	99·50	2·82
II.	0·09	0·13	—	5·93	99·40	2·73

L. J. S.

The Eulysite of Södermanland. John Palmgren (*Bull. Geol. Inst. Univ. Upsala*, 1917, **14**, 109—228).—Eulysite is a dark, fine-grained olivine-augite-garnet rock occurring as beds in gneiss at Tunaberg and several other places in central Sweden. It is

usually classed with the peridotites and sometimes with eclogite; the present author regards it as a crystalline schist. The following minerals were isolated from the rock for optical examination by the Fedorov "universal method." The olivine is a manganfayalite; analysis I is of honey-yellow grains picked out from the crushed rock from Gillinge, and II of the portion soluble in dilute hydrochloric acid of the rock from Tunaberg. Diopside from the Gillinge rock gave III, corresponding with $CaMgSi_2O_6$ 19%, $CaFeSi_2O_6$ 61%, and $MgFeSi_2O_6$ 20%. Iron-anthophyllite (IV) from Tunaberg shows a distinct prismatic amphibole cleavage and straight extinction; birefringence, negative, $\gamma-\alpha=0{\cdot}020$, optic axial angle $2V=89°6'$. The analysis corresponds with $3FeSiO_3+RSiO_2$, where R = Mg, Mn, Ca. The mineral is very similar to that from Rockport, Massachusetts (Warren, A., 1904, ii, 45). Analysis V is of hornblende from Gillinge. Grünerite, from Strömshult, Tunaberg, with extinction angle $(c:\gamma)=14{\cdot}5°$, gave VI, corresponding with $FeSiO_3+RSiO_3$. The relation of this to other monoclinic iron amphiboles is discussed. VII of potash–felspar, mainly microcline with some orthoclase, from Gillinge. Garnets at Tunaberg are represented by almandine (anal.

	SiO_2.	TiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.	Total.	Sp. gr.
I.	28·22	—	—	—	63·20	5·19	0·50	2·32	—	—	—	99·43	4·32
II.	31·62	—	0·46	—	35·12	26·51	1·58	4·39	—	—	—	100·00	—
III.	49·84	—	0·78	0·50	19·85	3·66	6·90	18·42	—	—	0·35	100·30	3·544
IV.	47·46	0·03	0·14	0·34	42·34	3·88	1·05	5·05	—	—	0·07	100·25	3·83
V.	37·30	0·93	12·75	7·18	18·73	1·42	11·46	4·94	2·87	0·96	1·22	99·93*	3·35
VI.	50·79	0·07	0·55	0·84	30·64	5·93	1·42	7·87	—	—	1·87	99·98	3·396
VII.	65·15	—	18·14	0·57	—	trace	0·08	trace	14·08	1·27	0·41	100·19†	2·595
VIII.	37·21	0·02	19·37	2·56	23·48	11·04	5·75	0·58	—	—	0·15	100·16	4·115
IX.	37·11	0·10	19·68	1·93	7·72	26·45	6·39	0·75	—	—	0·11	100·24	4·09
X.	47·92	—	0·16	0·46	13·78	27·96	6·20	3·58	—	—	0·28	100·34	3·60

* Also F, 0·17. † Also BaO, 0·49.

VIII) and spessartite (IX); the former is intermediate in composition between typical almandine and spessartite, and is called manganalmandine. Veins in a richly manganiferous eulysite at Tunaberg are filled with a pyroxenic mineral (named *sobralite*), together with manganfayalite and spessartite. In hand-specimens the former is brown with a lilac tinge. Analysis X is of opaque, pale lilac grains, and corresponds with $4MnSiO_3$, $2FeSiO_3$, $CaSiO_3$, $MgSiO_3$. Optical examination shows it to be triclinic with cleavages in three directions, and to differ from pyroxmangite (Ford and Bradley, A., 1913, ii, 869) in the position of the optic axial plane. Analyses, also by R. Mauzelius, are given of the rock and of the associated iron-ores and limestones. L. J. S.

Analytical Chemistry.

Ring Formation in Reactions. F. Reiss and G. Diesselhorst (*Chem. Zeit.*, 1919, **43**, 39).—Certain reactions, such as the blue coloration given by nitrates with diphenylamine and sulphuric acid, are characterised by the formation of a ring, preceding the production of a coloured zone. This is due to adhesion between the liquid and the glass of the tube, and the greater the surface of contact the more sensitive is the reaction. C. A. M.

Use of Filter-paper Pulp in Analysis. O. Hackl (*Chem. Zeit.*, 1919, **43**, 70—71).—The addition of a quantity of filter-paper pulp is advantageous in the filtration of such precipitates as barium sulphate, calcium oxalate, sulphur, ferric hydroxide, aluminium hydroxide, etc., but it should not be used in the last two instances when it is desired to re-dissolve the precipitates in hot hydrochloric acid. A precipitate of ferric hydroxide mixed with filter-paper pulp, when ignited, forms a finely divided powder which dissolves readily in hydrochloric acid. In the case of filtration of silica from a solution containing aluminium salts, the presence of filter-paper pulp retards the rate of filtration. [See, further, *J. Soc. Chem. Ind.*, 1919, 235A.] W. P. S.

The Replacement of Platinum by an Alloy in Apparatus for Electrolytic Analysis. Paul Nicolardot and Jean Boudet (*Bull. Soc. chim.*, 1919, [iv], **25**, 84—86. Compare A., 1918, ii, 425).—For the preparation of cathodes, the authors recommend the use of an alloy of gold and copper in the proportion of 9:1 in place of platinum. The total loss in weight of such a cathode, weighing 23·5 grams, was only 0·001 gram during twenty estimations of different types. Anodes may be prepared from the same alloy, but should be coated with a thin layer of platinum electrolytically deposited. W. G.

Apparatus. H. Vigreux (*Ann. Falsif.*, 1918, **11**, 385—387).—*Apparatus for the Estimation of Ammonia.*—The distillation flask is connected with a vertical fractionating column, the upper part of which is connected with a slightly inclined condensing apparatus. The latter condenses the steam, and the greater part of the condensed water returns through the column into the flask, whilst the ammonia vapours pass to an absorption vessel. *Safety Valve for Water Pumps.*—The valve, which is placed between the pump and the vessel from which the air is to be exhausted, consists of a vertical chamber containing a float; if water flows back from the pump and enters the lower part of the chamber, the float rises and cuts off connexion with the other portions of the apparatus. *Condenser.*—Numerous cross tubes are provided in the inner tube

of an ordinary Liebig condenser; these tubes provide a free passage for the water in the jacket and increase the available condensing surface. [See, further, *J. Soc. Chem. Ind.*, 1919, 200A.]

W. P. S.

Absorption Pipettes. E. VAN ALSTINE (*J. Ind. Eng. Chem.*, 1919, **11**, 51—52).—Two vertical cylindrical bulbs, placed one above the other, are connected by a short length of glass tubing, the centre portion of which is constricted to a capillary. A side-tube connects the top of the upper bulb with the tube below the capillary. The bottom of the lower bulb is, by a swan-neck tube, connected with the top of a third bulb, and this, in turn, with a fourth bulb. For use, the absorption solution contained in the fourth bulb is drawn over so as to fill the two cylindrical bulbs; the gas (for example, air containing carbon dioxide) is admitted from the measuring burette into the top of the upper bulb and passes into the lower bulb through the side-tube. Meanwhile, the solution passes gradually through the capillary and continually wets the interior wall of the lower bulb, which now contains most of the gas. Some absorption also takes place in the third bulb, the fourth bulb serving as a reservoir for the solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 201A.] W. P. S.

Simplified Gas Analysis: Burette without Stopcocks for Gas Analysis. J. J. R. MACLEOD (*J. Lab. and Clin. Med.*, 1918, **4**, 69—72; from *Physiol. Abstr.*, 1919, **3**, 553—554).—The apparatus is designed for teaching purposes, and is based on that of Haldane. The chief differences are that it has screw clips instead of stopcocks, and a special "pressure adjuster" to adjust the gas pressure in the burette after the screw clips have been tightened.

W. G.

Method for the Extraction and Estimation of Dissolved Gases in Water. F. W. RICHARDSON (*J. Soc. Chem. Ind.*, 1919, **38**, 32—33T).—A strong glass bottle of about 1 litre capacity is filled with the water. The lower tube of a bulb or funnel provided with two taps is passed through a rubber stopper, the air is exhausted from the bulb, and the stopper is inserted in the bottle, thereby connecting the tube with the water. When the tap is opened a small quantity of the water enters the bulb, evolution of gas at once begins, and, if the bottle is placed in water at about 40° and the gases removed occasionally from the bulb, the water will continue to boil until all the gases have been expelled and collected. W. P. S.

Estimation of Chlorate and Perchlorate in Potassium Nitrate. A. WOGRINZ and J. KUBER (*Chem. Zeit.*, 1919, **43**, 21—22).—The methods described by Förster (A., 1899, ii, 57), Tschernobéev (A., 1905, ii, 416), Winteler (A., 1898, ii, 90), and Hendrixson (A., 1904, ii, 679) were found to be trustworthy.

W. P. S.

Rapid Method of Estimating Sulphide Sulphur in Pyrites. A. Bartsch (*Chem. Zeit.*, 1919, **43**, 33—34).—On heating pyrites with hydrobromic acid in the presence of metallic mercury the whole of the sulphide sulphur is liberated as hydrogen sulphide. Air is expelled from the apparatus, and the last traces of hydrogen sulphide afterwards driven forward by means of a current of carbon dioxide. The hydrogen sulphide is absorbed in an acetic acid solution of cadmium acetate or of zinc acetate and cadmium acetate, and is subsequently estimated by an iodometric method. [See also *J. Soc. Chem. Ind.*, 1919, 171A.] C. A. M.

Estimation of Phosphorus in Vanadium Steels, Ferrovanadium, Non-vanadium Steels, and Pig Iron. Chas. Morris Johnson (*J. Ind. Eng. Chem.*, 1919, **11**, 113—116).—The methods here described make use of a faintly ammoniacal ammonium molybdate solution, which is easy to prepare and convenient to handle, and keeps clear indefinitely. The true phosphorus content of ferrovanadium containing as much as 56·7% of vanadium may be estimated. [See, further, *J. Soc. Chem. Ind.*, 1919, 179A.] T. H. P.

Organic Phosphorus of Soil: Experimental Work on Methods for Extraction and Determination. J. C. Schollenberger (*Soil Sci.*, 1918, **6**, 365—395. Compare Potter and Benton, A., 1917, i, 76).—Very full details are given for the estimation of inorganic phosphorus and total phosphorus in the soil, using Neumann's wet combustion for the latter. For the preliminary removal of bases, prior to the extraction of organic phosphorus, it is recommended to wash the soil with 1% hydrochloric acid until 50 c.c. of the extract no longer contains any calcium, after which the acid is washed out by means of a saturated solution of carbon dioxide. The residual soil is then extracted with 4—6% ammonium hydroxide, using 400 grams of soil per litre and shaking two to eight hours, the extract being subsequently filtered through a layer of the soil on a Buchner funnel, this process taking one to three days, and being the most satisfactory for the removal of clay from the extract. Sodium or potassium hydroxide is no more efficient than ammonium hydroxide in extracting organic phosphorus from the soil, and one extraction by the latter alkali, using the proper procedure, removes from the soil practically all the organic phosphorus that is capable of being taken into solution.

No constant relation was observed between total organic matter and organic phosphorus in the ammoniacal extracts, although, as a general rule, they varied in the same direction. For a given soil, it was found that the humus and organic phosphorus in, and the colour of, the ammoniacal extracts, and the total nitrogen content of the soil in the four layers, 0—6 in., 6—12 in., 12—18 in., and 18—24 in., are present in the same relative proportions in each layer. W. G.

The Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. J. Clarens (*Bull. Soc. chim.*, 1919, [iv], **25**, 87—90. Compare A., 1918, ii, 128).—A reply to Villiers (compare A., 1918, ii, 333). W. G.

Estimation of Boric Oxide in Glass. J. D. Cauwood and T. E. Wilson (*J. Soc. Glass Tech.*, 1918, **20**, 246—252).—Sullivan and Taylor's modification (*Chem. News*, 1915, **111**, 64) of Wherry's method (A., 1910, ii, 92) yields trustworthy results in all cases, whilst Wherry's method itself is untrustworthy when the glass contains much zinc or lead. In the modified method, the sodium carbonate fusion is dissolved in water, the insoluble zinc, lead, etc. carbonates are removed by filtration, and the filtrate then acidified and treated as in Wherry's method. W. P. S.

Micro-elementary Analysis of Organic Substances. J. V. Dubsky (*Helv. Chim. Acta*, 1919, **2**, 63—75).—A description of the methods of estimating carbon, hydrogen, and nitrogen by micro-analysis. The advantages of a new micro-balance, by P. Hermann, are enumerated. C. S.

Microelementary Analysis of Compounds containing Sulphur, Halogens, and Oxidised Nitrogen. Double Combustion. Ch. Gränacher (*Helv. chim. Acta*, 1919, **2**, 76—84).—To avoid obtaining high results in the estimation of carbon in organic compounds containing sulphur and halogens, and particularly in highly nitrated substances, the author employs a layer of lead peroxide 5 cm. in length at the forward end of the combustion tube beyond the silver roll. The lead peroxide must be maintained at a temperature between 170° and 180°, and this is secured by surrounding this portion of the combustion tube with a copper chamber containing boiling aniline.

A "universal tube" suitable for the combustion of any substance obtained in the organic laboratory is one filled from the boat forwards with (1) silver roll, (2) mixture of equal parts of copper oxide and lead chromate, (3) silver roll, and (4) lead peroxide.

Arrangements of apparatus are described whereby the estimation of the nitrogen or of the carbon and the hydrogen in two substances in two tubes side by side can be performed simultaneously. C. S.

The Red Iodotannic Reagent. D. E. Tsakalotos and D. Dalmas (*Bull. Soc. chim.*, 1919, [iv], **25**, 80—84).—The sensitiveness of the iodotannic reaction (compare A., 1918, ii, 454) is much greater than that of starch-iodide, especially for very dilute solutions of iodine, but the reaction is interfered with by the presence of potassium iodide, which, on the other hand, increases the sensitiveness of the starch-iodide. An excess of either iodine or tannin inhibits the formation of the red colour in the iodotannic reaction. W. G.

Estimation of Cadmium by the Hydrogen Sulphide Method. Edward Schramm (*J. Ind. Eng. Chem.*, 1919, **11**, 110—113).—The literature of the estimation of cadmium and the general considerations governing it are discussed, and a method described which permits of the accurate estimation of cadmium in brass. [See *J. Soc. Chem. Ind.*, 1919, 181A.] T. H. P.

A Very Sensitive Reaction of Copper. Application to the Analysis of Ashes and of Arable Soils. L. Maquenne and E. Demoussy (*Compt. rend.*, 1919, **168**, 489—492).—When potassium ferrocyanide is added to a very dilute solution of copper chloride in hydrochloric acid in the presence of a zinc salt so that the copper and zinc are in the proportion of 1:4 or 5, the liquid is first tinged yellowish-red, but gradually a precipitate forms which when separated is seen to be blue. This is a very delicate test for copper in the absence of iron, manganese, or nitric acid, and may be applied to the detection and estimation of traces of copper in plant ashes if the copper is first separated electrolytically. [See *J. Soc. Chem. Ind.*, 1919, 235A.] W. G.

Estimation of Iron in Ores by Permanganate. Robert Schwarz and Bernhard Rolfes (*Chem. Zeit.*, 1919, **43**, 51).—In the estimation of ferrous chloride in hydrochloric acid solution a mixture of manganese sulphate and phosphoric acid is added to inhibit the oxidation of the hydrochloric acid by the permanganate. This, however, is not perfectly effective; the results are always high, and hitherto it has been customary to correct this error by standardising the permanganate under the conditions under which it is used in the titration, thereby employing a false standardisation value. The authors have found that colloidal silicic acid exerts a perfect protective action, when used in addition to the manganese sulphate and phosphoric acid mixture, and that correct results are then obtained with permanganate standardised by any of the usual methods. About 4—5 grams of the ore are dissolved in 40—60 c.c. of boiling, strong hydrochloric acid, and the solution made up to 500 c.c. Fifty c.c. of the liquid are reduced with stannous chloride, the excess of the latter removed by mercuric chloride, 10 c.c. of the manganese sulphate and phosphoric reagent are added, and about 5 c.c. of a solution of "water-glass," D 1·17, 1 c.c. of which contains about 0·1 gram of SiO_2. The silicic acid must not separate in a flocculent condition, but remain in colloidal solution; the titration with permanganate should be made without delay. If the reduction of the iron be effected in another manner and no mercurous chloride be present, the silicic acid alone is capable of inhibiting the oxidation of the hydrochloric acid in the same way as the manganous salt. J. F. B.

The Estimation of Zirconium. Paul Nicolardot and Antoine Reglade (*Compt. rend.*, 1919, **168**, 348—351).—Zirconium is quantitatively precipitated either in neutral solution or in the presence of sulphuric acid, up to 20% of acid, by the addition

of ammonium phosphate, the precipitate being calcined, ignited, and weighed as the pyrophosphate, using the factor 0·487 for converting the weight of pyrophosphate into weight of oxide. This method may be used for the separation of zirconium from iron, chromium, and aluminium. In the presence of iron and chromium an acidity equal to 20% sulphuric acid is necessary to keep up these two metals, but if aluminium is the only other metal present 10% acid is sufficient. W. G.

A Microchemical Reaction for Gold, Silver, and Rubidium (Cæsium). Friedrich Emich (*Monatsh*, 1918, **39**. 775—776).—Blood-red crystals are formed when solutions of gold chloride are brought into contact with silver chloride and rubidium chloride; these can be employed in the detection of the three metallic ions. The place of rubidium may be taken by cæsium and probably by potassium. The new salts appear to be comparable with the well-known triple nitrites, and, like the latter, promise to be useful in micro-analysis. H. W.

The Estimation of the Methoxyl Group. John Theodore Hewitt and William Jacob Jones (T., 1919, **115**, 193—198).

[Estimation of Methoxyl Groups.] M. Hönig (*Monatsh.*, 1918, **39**, 871—872).—In a recent communication (Hönig and Spitzer, A., 1918, i, 375), a method of estimating methoxy-groups in substances containing sulphur has been described in which the methyl iodide and hydrogen sulphide are absorbed in pyridine containing silver nitrate, and the estimation is completed after removal of the silver sulphide; the procedure was erroneously designated as a modification of the method of Kirpal and Bühn, who, however, employed pure pyridine only. Further details with respect to the accuracy of the new method are promised in a subsequent communication. H. W.

Estimation of the Geraniol Content of Citronella Oil. A. W. K. De Jong (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 576—581).—The method for the estimation of geraniol in citronella oil given in Schimmel & Co.'s Bericht (A., 1900, ii, 175; 1912, i, 880) is based on quantitative esterification of the geraniol by phthalic anhydride, and this the author finds to be impossible of attainment, although with mixtures of geraniol and citronellal this method gives results differing but little from the true values; the amount of citronellal esterified by phthalic anhydride increases with that of the geraniol present. Similarly, the esterification of citronellal by means of acetic anhydride is increased by the presence of either acetic acid or geraniol, but complete esterification is here not possible without the use of sodium acetate. T. H. P.

Modifications of Benedict's and Folin's Quantitative Sugar Methods. Howard D. Haskins (*J. Biol. Chem.*, 1919, **37**, 303—304).—In using Benedict's method (compare A., 1911,

ii, 340), sodium thiocyanate may replace potassium thiocyanate in preparing the solution if 105 grams of the former salt are used in place of 125 grams of the latter. In Folin's modification (compare A., 1918, ii, 207) of this method, the author recommends for the mixture of salts 20 grams of sodium thiocyanate, 60 grams of anhydrous sodium carbonate, and 100 grams of disodium hydrogen phosphate, using 4 grams of this mixture for each estimation, and boiling for only half the time recommended by Folin. W. G.

Titration of Sugars by Rupp and Lehmann's Method. E. SCHOWALTER (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 180—187).—This method (A., 1909, ii, 442) yields trustworthy results only when carried out under the exact conditions as to concentration of the solutions, etc., employed in constructing the sugar tables used for reference. In the iodometric titration of the excess of copper, an aliquot portion of the solution should be taken if the amount of unreduced copper is large. [See, further, *J. Soc. Chem. Ind.*, 1919, April.] W. P. S.

Estimation of Soluble Starch in the Presence of Starch and its Hydrolytic Cleavage Products. JAMES CRAIG SMALL (*J. Amer. Chem. Soc.*, 1919, **41**, 107—112).—The method is based on the insolubility of the blue iodine compound of soluble starch in the presence of a half-saturated solution of ammonium sulphate. Three grams of the sample are dissolved by suspending in 200 c.c. of water and heating to the boiling point. The liquid is made up to 250 c.c., and the unconverted starch removed by filtration or centrifuging; 200 c.c. of the filtrate are then treated with 10 c.c. of a 4% solution of iodine in 6% potassium iodide solution, and an equal volume of saturated ammonium sulphate solution is added. The flocculent precipitate is consolidated in the centrifuge, the clear liquid siphoned off through a filter, and the precipitate is washed about five times by shaking with water, adding an equal volume of saturated ammonium sulphate solution, and centrifuging each time. The washing is continued until the brown coloration due to erythrodextrin has been removed. The blue precipitate in the centrifuge bottle, and any minor portion of it which has been collected on the filter, are washed into a flask with a total volume of water not exceeding 300—400 c.c., and dissolved by boiling, after the addition of 5 c.c. of hydrochloric acid, D 1·125; the iodine is driven off, and the starch is completely saccharified by adding a further 20 c.c. of acid and heating in the boiling water-bath for four hours. The dextrose is determined polarimetrically and calculated as starch. This method gives accurate results, even in the presence of large proportions of dextrins. It is to be noted that the violet iodine compound of amylodextrin is also precipitated by ammonium sulphate if an excess of iodine is present; it is dissolved, however, in the course of the washing, after the excess of iodine has been removed. Amylodextrin may therefore be determined by difference, washing by the above method in the one case,

and with the addition of excess of iodine solution to each wash water in the other. J. F. B.

Glycogen Estimation. I. Yamakawa (*Tokyo. Igak. Zasshi*, 1917, **31**, 47—68; from *Physiol. Abstr.*, 1919, **3**, 516).—The tissue is heated with potassium hydroxide at 120°, cooled, neutralised with hydrochloric acid, and then hydrolysed with the same acid. The protein is removed by means of colloidal ferric hydroxide and the dextrose estimated. The removal of the protein is essential, as it acts as a protective colloid. The results obtained in this manner are higher than those by previous methods. W. G.

Simple Method for the Determination of the Digestibility of the Cellulosic Part of Vegetable Fibres, especially of Woody Fibres. P. Waentig and W. Gierisch (*Zeitsch. physiol. Chem.*, 1918, **103**, 87—103).—Recent research on woody matter has shown that thorough removal of the lignified substance from the fibres is necessary in order to obtain material of a moderately high degree of digestibility. The authors have devised a simple method for obtaining rapidly an approximate measure of the non-saccharifiable, and therefore undigestible, material, which interferes with the digestion of the nutrient constituents in woody substances. This method is based on the fact that, when chlorine acts on woody fibre, the lignin is at first almost exclusively attacked, the proportion of lignin present corresponding with that of the chlorine absorbed. By "chlorine number" is understood the percentage increase in weight, calculated on dry matter, occurring when the woody material is subjected under certain definite conditions to the action of a current of moist chlorine. As a general rule, the chlorine number and indigestibility increase or diminish together. [See *J. Soc. Chem. Ind.*, 1919, 195A.] T. H. P.

The Test for Tartrates Depending on the Formation of the Copper Tartrate Complex. L. J. Curtman and B. R. Harris (*J. Amer. Chem. Soc.*, 1919, **41**, 207).—The statement made by Curtman, Lewis, and Harris (A., 1918, ii, 87) that comparatively small amounts of phosphates or borates, when treated according to Böttger's procedure ("The Principles of Qualitative Analysis," 1906, 159), respond in the same way as tartrates, is now found to be incorrect; neither of these anions, even in amounts as high as 0·5 gram, gives a blue filtrate. T. H. P.

Fat Extraction Apparatus. E. Griffiths-Jones (*Analyst*, 1919, **44**, 45—47).—An extraction flask is attached in the ordinary way by means of a cork to the lower end of a vertical condenser. The material to be extracted is packed into an extraction thimble which is fitted on to the lower end of the condenser tube, the thimble being thus inside the neck of the flask. The vapours of the solvent contained in the flask are conducted through a side-tube which passes just through the cork closing the flask,

and extends upwards and parallel with the condenser to the top of the latter, and then passes down the condenser tube to approximately the level of the water-intake. The condensed solvent falls into the thimble and passes back again into the flask. [See, further, *J. Soc. Chem. Ind.*, 1919, 201A.] W. P. S.

Estimation of "Saccharin" in Tablets. A. Bonis (*Ann. Falsif.*, 1918, **11**, 369—372).—Free sodium hydrogen carbonate is estimated in the tablets by titration with *N*/10-sulphuric acid, using methyl-orange as indicator. The quantity of "saccharin" is found by fusing a portion of the sample with a mixture of sodium carbonate and sodium nitrate, and estimating the sulphate formed; the amount of barium sulphate obtained is calculated into sodium "saccharinate." Free "saccharin" may be present, and is estimated by extraction with ether; in this case, the sodium "saccharinate" remains insoluble, and its quantity may be determined by the fusion method mentioned. Lactose, if present, is estimated separately. *p*-Sulphaminobenzoic acid is detected in the tablets by hydrolysing the sample with hydrochloric acid, concentrating the solution to a small volume, and placing it aside for twenty-four hours; the para-acid crystallises out, and may be collected and weighed. [See, further, *J. Soc. Chem. Ind.*, 1919, 198A.] W. P. S.

Analysis of Commercial "Saccharin." II. Detection and Estimation of Impurities. H. Droop Richmond and Charles Alfred Hill (*J. Soc. Chem. Ind.*, 1919, **38**, 8—10T. Compare A., 1918, ii, 339, and Procter, T., 1905, **87**, 242).—The methods described deal with the following impurities and properties: *Moisture. Mineral matter.* p-*Sulphonaminobenzoic acid.*—1·5 Grams of "saccharin" are heated with 10 c.c. of 70·5% sulphuric acid so that the liquid boils in as nearly as possible one minute, and then boiled for exactly thirty seconds, the solution being then poured at once into 15 c.c. of distilled water kept cool by immersion of the vessel in cold water; after mixing, the solution is cooled under the tap, seeded with a trace of the para-acid, and placed in ice-water. If present to the extent of 1%, para-acid crystallises out in thirty minutes or less; if 3% is present, the crystals usually begin to separate before seeding on cooling, and when about 10% is present, the acid begins to crystallise in the hot. o-*Sulphonaminobenzoic acid.* o-*Toluenesulphonamide.*—This dissolves in sodium hydrogen carbonate, whilst "saccharin" is insoluble. *Lead. Arsenic. Ammonia. Easily carbonisable organic matter.*—The test of the British, French, and U.S. Pharmacopœias may be replaced by the coloration obtained in the test for para-acid with 70·5% sulphuric acid (see above). *Sweetness. Melting point.*—Pure "saccharin" has m. p. 229°. *French Codex identification test.*—When heated in a test-tube with a small crystal of resorcinol and several drops of concentrated sulphuric acid, "saccharin" gives a liquid at first reddish-yellow and then dark green. Treatment of the cooled liquid with water and supersaturation with

sodium hydroxide gives a liquid showing intense green fluorescence. This test is, however, not characteristic of "saccharin," since the ortho-acid gives the same result, and the amide a moderate fluorescence. T. H. P.

Microchemical Identification of Stovaine and Cocaine. DENIGÈS (*Bull. Soc. Pharm., Bordeaux*, 1917; from *Ann. Chim. anal.*, 1919, [ii], **1**, 65—66).—The tests described are carried out on a microscope slide, a small drop of the solution being treated with a drop of the reagent. Platinum chloride does not give a precipitate with a 0·5% stovaine hydrochloride solution, but a fine, granular precipitate is obtained with a 1% solution; in the case of cocaine hydrochloride solution of either of the above concentrations, a characteristic, crystalline precipitate is formed. Gold chloride gives a crystalline precipitate with both alkaloids, but the form of the crystals is quite different for the two salts. Picric acid yields a yellow, crystalline precipitate with stovaine hydrochloride, whilst cocaine picrate is amorphous and changes to yellow, liquid droplets when stirred. [See, further, *J. Soc. Chem. Ind.*, 1919, 198A.] W. P. S.

Estimation of Morphine in Complex Products. III. Opium and Mixtures containing Opium. ALFRED TINGLE (*Amer. J. Pharm.*, 1918, **90**, 851—861. Compare this vol., ii, 87, 88).—The presence of resinous matters in opium interferes with the estimation of morphine by the methods described previously (*loc. cit.*); the greater part of these resins may be separated by heating the slightly alkaline solution containing them, together with the morphine, with an excess of salicylic acid. When the mixture is cooled, the resin is precipitated, and may be removed by filtration. The morphine is then precipitated from the filtrate, collected, redissolved, extracted with alcohol–chloroform mixture, and titrated. [See, further, *J. Soc. Chem. Ind.*, 1919, 116A.] W. P. S.

New Titration Method for the Determination of Uric Acid in Urine. J. LUCIEN MORRIS (*J. Biol. Chem.*, 1919, **37**, 231—238).—A slight modification of the method described for the estimation of uric acid in blood (compare A., 1918, ii, 251). W. G.

[**Detection of Traces of Blood Pigment.**] JOHN ALEXANDER MILROY (*Biochem. J.*, 1918, **12**, 327—329).—See this vol., i, 179.

Impurity in Ethyl Ether giving a Blue Coloration with Benzidine. F. WEEHUIZEN (*Pharm. Weekblad*, 1919, **56**, 301—303.)—Attention is directed to the presence in some samples of ethyl ether used for analytical purposes of an impurity which gives a blue coloration on addition of hydrogen peroxide and benzidine. Pieces of potassium hydroxide kept in the ether for a time are sufficient to remove the impurity. W. S. M.

The Value of Walker's Method of Estimating Casein in Milk. A. Agrestini (*Staz. sper. agr. Ital.*, 1917, **50**, 109—114; from *Chem. Zentr.*, 1918, ii, 866).—Comparisons of the rapid method devised by Walker (A., 1914, ii, 309) with the process of Schlossmann and von Bondzinski show the former to be very convenient, but not completely trustworthy. The amounts of alkali required to produce neutrality in Walker's procedure after addition of formalin are either identical with or very near to those required in the direct titration of the original milk. This result appears to support the view of Bordas and Touplain (A., 1911, ii, 631) that the acidity of fresh milk depends mainly on the casein, and allows an approximate estimation of the latter by simple titration in the presence of phenolphthalein as indicator. H. W.

Vernes' Method (Sero-diagnosis of Syphilis). Roger Douris and Robert Bricq (*Bull. Soc. chim.*, 1918, [iv], **23**, 472—478. Compare Vernes, *Compt. rend.*, 1917, **165**, 769; 1918, **166**, 575; **167**, 383).—Vernes has shown that serum in the presence of an inorganic or organic colloidal suspension causes a periodic precipitation, the rhythm of which differs according as the serum is normal or syphilitic, and that it is possible to prepare a fine organic suspension of a determined stability which will flocculate with a certain dose of syphilitic serum, but not with the same dose of normal serum. The authors give full details for carrying out the test, using red globules from sheep's blood, pig serum, and "perethynol" (an absolute alcoholic extract of dried, powdered, and de-fatted horse-heart muscle), and measuring, not the flocculation, but the hæmolysis colorimetrically. W. G.

Estimation of Acidity and Titratable Nitrogen in Wheat with the Hydrogen Electrode. C. O. Swanson and E. L. Tague (*J. Agric. Res.*, 1919, **16**, 1—15).—Aqueous extracts of wheat were made at 5°, 20°, 40°, and 50°, the mixture being shaken for times varying from five minutes to twenty-four hours. The hydrogen-ion concentration of the extract as measured by the hydrogen electrode is practically independent of the temperature and the duration of the extraction, but the volume of $N/20$-barium hydroxide solution necessary to add to bring the extract to a definite P_H value increases with the time of shaking, and within certain limits is proportional to it. As the duration increases, the volume of standard alkali required increases up to a limit, which is reached sooner as the temperature of extraction rises. This phenomenon is due to the presence in the extract of substances which only become ionised when an alkali is added.

The amino-nitrogen, as determined by Sörensen's formaldehyde method, is all extracted in two hours at 40°. The amount of phosphorus in the extract made at 20° directly precipitable by magnesia mixture is about one-half of the total phosphorus present, but at 40° practically the whole of the phosphorus is converted into a form which is precipitated by magnesia mixture. W. G.

General and Physical Chemistry.

Matter and Light. Attempt at the Synthesis of Chemical Dynamics. Jean Perrin (*Ann. Physique*, 1919, [ix], **11**, 5—108).—A purely theoretical discussion in which the author endeavours to show that it is possible to develop a coherent theory, which sees in light the cause of chemical reactions, and which elucidates and correlates varied types of phenomena which at first sight seem quite different. According to the theory, dissociation or combination, phosphorescence, radioactivity, change of physical state, all obey one and the same fundamental law, which is connected with the internal structure of the atom. W. G.

Dispersion of Diamond. L. Silberstein (*Phil. Mag.*, 1919, [vi], **37**, 396—406).—A mathematical paper in which the conception of electrical interaction of atoms is applied to the refractive properties of diamond, considered as a known assemblage of fixed atomic centres, each containing a single dispersive electron and becoming a doublet in the presence of an external electric field. J. F. S.

Regularities of the Second Kind in Line Spectra. J. E. Paulson (*Zeitsch. wiss. Photochem.*, 1918, **18**, 202—208).—The author, following the lead of Kayser, terms regularities between the wave-lengths of the various spectrum lines, regularities of the second kind. The present paper is a theoretical discussion of these regularities, in which it is shown that the magnetic resolution of the lines of a wave-length system does not follow such simple laws as that of the series lines. J. F. S.

Vacuum Arc Spectra of Various Elements in the Extreme Ultra-violet. J. C. McLennan, D. S. Ainslie, and D. S. Fuller (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 316—332. Compare this vol., ii, 125).—A vacuum arc spectrograph is described, together with the method of operation. The vacuum arc spectra of copper, aluminium, zinc, carbon, iron, tin, thallium, lead, nickel, cobalt, and cadmium have been measured down to $\lambda=1400$. The wave-lengths are compared in all cases with values obtained by other observers, and the intensities and frequencies are included in all the tables. In the case of zinc, the lines $\lambda\lambda=2025{\cdot}5(16)$, $1821{\cdot}8(3)$, $1589{\cdot}6(10)$, $1510{\cdot}4(1)$, $1491{\cdot}5(1)$, $1486{\cdot}2(6)$, $1478{\cdot}5(2)$, $1477{\cdot}6(4)$, $1457{\cdot}9(4)$, $1457{\cdot}5(4)$, $1451{\cdot}1(4)$, $1445{\cdot}0(3)$ were measured. The figures in brackets represent the intensities of the lines. For aluminium, the lines $\lambda\lambda=1989{\cdot}9(14)$, $1935{\cdot}1(4)$, $1930{\cdot}4(10)$, $1862{\cdot}8(32)$, $1854{\cdot}5(32)$, $1766{\cdot}6(4)$, $1761{\cdot}9(10)$, $1724{\cdot}3(10)$, $1720{\cdot}7(8)$, $1718{\cdot}5(4)$, $1670{\cdot}6(4)$, $1611{\cdot}8(14)$, and $1605{\cdot}6(12)$ were measured. In the case of copper, the lines $\lambda\lambda$ $2037{\cdot}3(6)$, $2026{\cdot}2(4)$, $2001{\cdot}0(4)$,

1979·6(4), 1748·6(4), 1739·7(4), 1721·8(6), 1708·5(4), 1704·9(2), 1693·4(4), 1692·5(1), 1686·7(4), 1684·6(2), 1681·7(1), 1679·1(2), 1674·6(2), 1671·5(2), 1670·1(2), 1651·9(2), 1642·1(8), 1594·2(8) were measured. The thallium arc was produced by placing metallic thallium in iron cups attached to iron poles; the lines measured in this case were λλ 1907·8(14), 1891·8(6), 1827·3(2), 1814·2(6), 1792·2(8), 1660·0(6), 1653·8(6), 1561·8(14), 1559·0(16), 1538·5(5), 1508·2(4), 1499·8(6), 1491·0(2), and 1478·0(4). With tin, the lines λλ 2152·5(12), 2041·2(2), 1941·0(1), 1899·8(20), 1831·4(6), 1811·2(20), 1756·6(16), 1741·3(1), 1699·5(10), 1489·2(6), 1475·2(15), 1438·3(4), 1437·3(4), 1402·4(4), and 1400·5(4) were observed. The lead arc was produced in the same way as that of thallium; the lines recorded in this case are 2170·5(8), 2060·5(8), 1925·8(2), 1913·7(4), 1904·2(2), 1898·7(2), 1895·5(2), 1821·7(14), 1796·5(10), 1744·2(1), 1741·1(2), 1726·2(10), 1682·5(12), 1671·6(12), 1597·6(3), 1555·8(12), 1511·7(4), 1494·7(1), 1492·7(1), 1434·0(5), and 1431·9. With a carbon arc, the lines λλ 2307·5(2), 2298·0(9), 2219·0(2), 2088·5(5), 1930·5(15), 1758·1(9), 1749·7(5), 1656·9(10), 1562·0(9), 1561·2(9), 1560·5(9), 1550·7(2), 1548·5(3), 1482·8(5), 1464·5(6) were recorded. A cobalt arc gave the lines λλ 2138·7(4), 2099·3(2), 2061·5(5), 2026·2(7), 1939·5(2), 1929·5(9), 1912·2(3), 1893·8(4), 1861·4(10), 1853·0(10), 1819·8(2), 1740·3(1), 1710·9(2), 1669·9(7), Mild steel electrodes were used for the production of the iron arc; the lines measured are λλ 2394·5(5), 2380·2(5), 2360·0(4), 2346·0(4), 2097·5(2), 2078·8(4), 2061·5(3), 1926·0(2), 1913·8(4), and 1894·3(3). In the case of nickel, forty-one lines lying between λ 2005·0 and λ 1650·1 were measured, but nothing of smaller wave-length than this. With the cadmium arc, the lines observed are λλ 1993·5(1), 1988·0(1), 1966·0(1), 1946·0(1), 1940·0(4), 1932·5(4), 1894·5(1), 1874·5(1), 1871·0(1), 1855·5(2), 1846·5(4), 1827·0(1), 1808·0(3), 1790·5(4), 1745·5(2), 1728·0(4), 1711·0(3), 1706·5(2), 1668·5(10), 1656·5(1), 1647·5(2), and 1526·5(1). Reproductions of photographs of the spectrograph and of all the spectra are appended to the paper. J. F. S.

Ultra-violet Light Absorption of Unsaturated Compounds. H. Ley (*Zeitsch. wiss. Photochem.*, 1918, **18**, 177—191).—The ultra-violet spectra of styrene, α-methylstyrene, β-methylstyrene, stilbene, methylstilbene, α-phenylstilbene, cinnamic acid, β-methylcinnamic acid, and α-phenylcinnamic acid have been investigated. In the case of styrene, a band is found at $1/\lambda = 4100$ ($c = 0{\cdot}001$, $d = 2$ mm.), and at ($c = 0{\cdot}01$, $d = 2{\cdot}5$—$7{\cdot}0$ mm.) bands occur at $1/\lambda = 3440$ and 3550. The introduction of a methyl group in the β-position displaces the original continuous absorption and the band 3440 toward longer wave-lengths, whilst the band 3550 vanishes. The introduction of a methyl group in the α-position brings about at higher concentrations a definite displacement toward the ultra-violet, and the absorption between 3400 and 3600 completely disappears. Stilbene possesses a deep band $1/\lambda = 3400$ ($c = 0{\cdot}001$ and $d = 1$—10 mm.); the introduction of a methyl group

into the ethylene group brings about a twofold change in the absorption spectrum: (i) a displacement of the continuous absorption towards the ultra-violet, and (ii) the bands are displaced in the same direction, or, in other words, at the position of maximum absorption the extinction coefficient is smaller. In the case of the derivatives of cinnamic acid, it is shown that β-methylcinnamic acid and α-methylstyrene are optically similar, whilst the same also applies to cinnamic acid and styrene. J. F. S.

Absorption Spectra of Acid Hæmatin, Oxyhæmoglobin, and Carbon Monoxide Hæmoglobin. A New Hæmoglobinometer. H. S. Newcomer (*J. Biol. Chem.*, 1919, **37**, 465—496).—Acid hæmatin has different spectral characteristics under varying conditions as to acid and solvent. The curve for material prepared in the manner described is constant and stable, for several days at least. The prominent band in the red has its deepest point at about 6620 Å.U. The other two bands in the visible spectrum are very shallow. There is a broad, general depression extending from 5100 to 5900 Å.U. which is divided by a very slight rise at 5480 Å.U. The great ultra-violet band of acid hæmatin is broader and shallower than in the case of oxyhæmoglobin, the broadening extending it further into the ultra-violet and obliterating the small peak at 3680 Å.U. which appears in the oxyhæmoglobin curve. There is beyond the peak at 3100 Å.U. a shallow but distinct band with its centre at 2780 Å.U. Beyond 2400 units, the absorption becomes very great. The further side of this band did not appear within the range of the instrument (2050 units). The β-band of oxyhæmoglobin is seen to be fainter than the α-band, but the difference in depth is slight. The great ultra-violet band is much deeper, the ratio of extinction coefficients being about eight. Oxyhæmoglobin has two further bands in the ultra-violet, at 3460 and 2760 Å.U., separated by a peak at 3100, somewhat higher than the corresponding one of acid hæmatin. The similarity in the ultra-violet of the absorption of the two substances would seem to indicate that it is due in large part to a radicle common to both. Carboxyhæmoglobin has an absorption similar to that of oxyhæmoglobin. In the visible, the bands are not so sharp and the transmission is not so great, particularly at the peak between the α- and β-bands. It is the lowness of this peak which accounts for the difference in shade between solutions of the two compounds. The visible bands of carboxyhæmoglobin are approximately of the same depth as the β-band of oxyhæmoglobin; they are shifted with respect to those of oxyhæmoglobin toward the violet; the great ultra-violet band is much deepened and shifted in the contrary direction. In the ultra-violet, the two peaks are higher than in the case of oxyhæmoglobin. The height of the peak at 3760 units and the depth of the band at 4190 units decrease very markedly with loss of CO from solution.

The amount of the extinction due to the admixed serum is only from one-fourth to one-seventh of the whole. The presence of

plasma can be neglected in discussing the visible absorption of these compounds. The blood in the superficial capillaries of the skin would be sufficient in quantity to absorb almost completely all the violet and ultra-violet light which might fall on it.

A "high transmission yellow" semaphore glass has an absorption curve which runs smoothly as a mean through the acid hæmatin curve.

The hæmoglobin value of this glass has been carefully estimated, and by this means a colorimetric method for the determination of hæmoglobin has been elaborated. A colorimeter of the Duboscq type is used. J. C. D.

A New Sector Spectrometer. Samuel Judd Lewis (T., 1919, **115**, 312—319).

Tyndallmeter for the Examination of Disperse Systems. Richard C. Tolman and Elmer B. Vliet (*J. Amer. Chem. Soc.*, 1919, **41**, 297—300).—An instrument is described for measuring the strength of the Tyndall beam in suspensions, colloidal solutions, smoke, and mists. It consists of a 6—8 volt lamp, a condensing lens, and a diaphragm through which the beam of light enters the chamber containing the gas or solution. The strength of the beam is then determined by a Macbeth illuminometer which has been standardised with either a suspension of finely divided silica or an opaque glass. J. F. S.

Relation between the Intensity of Tyndall Beam and Concentration of Suspensions and Smokes. R. C. Tolman, L. H. Reyerson, E. B. Vliet, R. H. Gerke, and A. P. Brooks (*J. Amer. Chem. Soc.*, 1919, **41**, 300—303. Compare preceding abstract).—The strength of the Tyndall beam has been determined after passing through silica suspensions and ammonium chloride smokes of various concentrations. It is shown that, in general, for liquid suspensions and smokes there is a strict proportionality between the concentration and the strength of the beam, provided that the concentration does not become high enough to give an opacity which affects the results, and that the size of the particles remains the same throughout the series of measurements.

J. F. S.

Disappearance of Smoke in a Confined Space. Richard C. Tolman, E. B. Vliet, W. McG. Pierce, and R. H. Dougherty (*J. Amer. Chem. Soc.*, 1919, **41**, 304—312. Compare preceding abstracts).—The gradual disappearance of smokes in confined spaces has been investigated. It is shown that a smoke disappears in an enclosed space owing to coagulation, to settling, and to the diffusion of the particles to the walls, where they adhere. The rate of disappearance was determined by means of a Tyndallmeter in boxes 1 cu. m. capacity with smokes of burning acetanilide, benzoic acid, and resin. The rate of disappearance is markedly increased by

stirring the smoke, owing to the fact that it was brought in contact with the walls, where it adhered. The finer the state of subdivision of the smoke particles, the higher the readings on the Tyndallmeter owing to the greater reflecting surface of the particles. The rate of disappearance of a finely divided smoke of a given concentration is greater than that of a coarse smoke of the same concentration owing to the increased opportunity for coalescence. In smokes of the same size of particles, the rate of disappearance increases with the concentration owing to the increased chances of coagulation and removal by the walls. Since the increased concentration and increased subdivision both lead to a higher rate of disappearance, it is impossible to raise the optical density of a smoke beyond a certain point by the introduction of more smoke material. J. F. S.

Rotatory Dispersive Power of Organic Compounds. IX. Simple Rotatory Dispersion in the Terpene Series. Thomas Martin Lowry and Harold Helling Abram (T., 1919, **115**, 300—311).

Principal Methods for the Determination of the Ionic Constitution of Solutions of Electrolytes and the Application of these to the Solution of Uranyl Nitrate. Léon Gómez (*Anal. Fis. Quím.*, 1919, **17**, 24—49).—A general discussion of the methods adopted to determine the mode of ionisation of an electrolyte in solution. With reference to the solution of uranyl nitrate, the results of the cryoscopic measurements of Dittrich (A., 1899, ii, 629) are examined. It is shown by extrapolation that the apparent molecular weight at infinite dilution is almost exactly one-third of the real molecular weight, so that an ionisation according to the scheme $UO_2(NO_3)_2 \rightleftharpoons UO_2^{\cdot\cdot} + 2NO_3'$ may be assumed. With increasing concentration, the ratio of the apparent to the real molecular weight approaches the value 2·5, so that even in concentrated solution the salt is ionised to a considerable extent, possibly in accordance with the equation

$$2UO_2(NO_3)_2 \rightleftharpoons U_2O_4^{\cdot\cdot\cdot\cdot} + 4NO_3'.$$

The values of the degree of dissociation, calculated on the assumption that the salt is a simple ternary electrolyte, are thus uncertain.

Dittrich's measurements of the equivalent conductivity show that up to an equivalent dilution of 4096 litres, the values of Λ do not converge to a limit. By forming the difference between each value of Λ and the next succeeding at double the dilution, it is shown that the difference decreases until the dilution $v = 64$ litres is reached. From this point, the difference increases progressively throughout the range of dilution considered. This behaviour is attributed to the progressive ionisation of the salt, according to the equations $UO_2(NO_3)_2 \rightleftharpoons [UO_2(NO_3)]^{\cdot} + NO_3'$ and

$$[UO_2(NO_3)]^{\cdot} \rightleftharpoons UO_2^{\cdot\cdot} + NO_3',$$

with subsequent hydrolysis at dilutions beyond $v = 64$ litres.

The transport numbers for the anion were determined at concentrations between 0·0024 and 0·074 mol. per litre, the fall in concentration of UO_2 at the anode being measured. The curve obtained resembles that for a typical ternary electrolyte, and shows a minimum at concentration 0·015 mol. per litre, indicating a maximum concentration of $[UO_2(NO_3)]'$. At concentrations beyond 0·07 mol., the transport number approaches unity, the "metallic" radicle now forming part of the anion. At concentrations lower than 0·01 mol., the presence of UO_2'' is indicated.

The addition of ammonia to a uranyl solution precipitated the compound $(NH_4)_2U_2O_7$. This indicates the probable presence of the anion U_2O_7'' in the solution. W. S. M.

Internally Complex Salts and Conjugated Salts of Alkali Metals. II. I. Lifschitz and Georg Beck (*Helv. Chim. Acta*, 1919, **2**, 133—143. Compare A., 1914, ii, 512).—In the earlier communication, it was shown that the alkali salts of oximinoketones and erythronitrolic acid have much lower electrical conductivities than the salts of simple acids in methyl-alcoholic or acetone solutions. It appeared at first sight that this abnormality was connected with the conjugated structure of the salts, which is superficially analogous to that of internally complex salts of the heavy metals. In the common cases of conjugated salts, no colour change accompanies electrolytic dissociation, and therefore it appeared to be of great interest to determine whether abnormal conductivity, in the above sense, is usual with such salts, as this would furnish a means of recognising conjugated structure. As far as solutions of the salts in methyl alcohol are concerned, it is found that conjugated structure causes no anomalies, which suggests that the peculiarities of the oximino-ketone salts require some other explanation.

The molecular conductivities of the sodium or potassium salts of the following compounds in methyl alcohol are recorded; hydriodic, acetic, propionic, butyric, valeric, benzoic, the three nitrobenzoic, benzenesulphonic, and *p*-phenolsulphonic acids, nitroethane, phenylnitroethane, *o*- and *p*-nitrophenylnitroethanes, the three nitrophenols, the five dinitrophenols, dinitroethane, phenyldinitromethane, nitroform, and phenylcyanonitromethane. These all show the same high conductivities, varying slightly with the nature of the cation, but free from abnormalities.

J. C. W.

Electrolytic Conductivity in Non-aqueous Solutions. III. Relations between the Conductivity of the Solute and several Physical Properties of the Solvent. Henry Jermain Maude Creighton (*J. Franklin Inst.*, 1919, **187**, 313—318).—The results obtained in a previous paper (this vol., ii, 44) for the electrical conductivity of *p*-tolyltrimethylammonium iodide in thirteen organic solvents are used in considering the relationship between conductivity, viscosity, and association. The formula suggested

by Jones, $\Lambda v'\eta/x$ = constant, where $\Lambda v'$ is the equivalent conductivity of comparable equivalent solutions and η and x are the coefficient of viscosity and the association factor of the solvent respectively, is found to hold approximately at 25° for acetone, propaldehyde, propionitrile, nitromethane, epichlorohydrin, benzaldehyde, formic acid, and anisaldehyde, the mean value being 0·33 and the extremes 0·242 and 0·391. Methyl and ethyl alcohols, and especially acetic acid (0·054), give lower values, and benzonitrile and nitrobenzene higher values. The expression $\Lambda_\infty\eta$, which Jones also showed to be constant, has a mean value for these solvents, except formic and acetic acids, of 0·56 at 25°. A comparison of the percentage dissociation of *p*-tolyltrimethylammonium iodide in the same solvents, at three different dilutions, with the dielectric constants (ϵ) of the solvents shows the latter to be only one factor in deciding the former; the amount of polymerisation of the solvent appears also to be an important factor. This is shown in the figures for methyl alcohol (ϵ = 32·5—34·8, x = 3·43) and nitrobenzene (ϵ = 33·4—37·4, x = 0·93), in which the percentage dissociations at a dilution of v = 128 are 79 and 66 respectively. Similar variations are found in the figures for propionitrile, benzonitrile, and epichlorohydrin. B. V. S.

Calculation of the Chemical Constants of Polyatomic Gases. Amélie Langen (*Zeitsch. Elektrochem.*, 1919, **25**, 25—45).—A theoretical paper in which the chemical constants of oxygen, nitrogen, nitric oxide, carbon monoxide, carbon dioxide, water, and ammonia are calculated for the normal condition, and the following values obtained: nitric oxide, +0·92; oxygen, 1·021—0·539; carbon monoxide, −0·04; nitrogen, −0·05; carbon dioxide, −0·406; water, −1·930; and ammonia, −2·454. The oxygen value was obtained from four different equilibria. The results were used to calculate the Einstein function of the specific heat β_v, and the values, hydrogen 430, ammonia 67·5, water 30, carbon dioxide 7·23, oxygen 0·736, and nitric oxide 0·543 obtained. The order of the frequencies is what is to be expected from the physical properties of the substances, and can be confirmed, as far as the order of the value is concerned, from the moment of inertia of these gases. J. F. S.

The Critical Temperature as a Single Function of the Surface Tension. Maurice Prud'homme (*J. Chim. Phys.*, 1918, **16**, 405—410).—The surface tension, γ, is connected with the temperature by the two equations $\gamma = a - bt$ and $\gamma^{\frac{2}{3}} = a' - b't$ (compare A., 1916, ii, 600), which at the critical temperature become $a - bt = 0$ and $a' - b't = 0$. It is found that, for substances which obey the Eötvös-Ramsay law, $t_c = \frac{1}{2}(t_1 + t_2)$ or $t_c = \frac{1}{2}(a/b + a'/b')$. This also holds good for liquefied gases. Amongst substances which do not obey the Eötvös-Ramsay law, the organic acids conform fairly closely to the above equation, whilst the alcohols, phenols, etc., obey the simple relationship $\gamma = a - bt$. W. G.

Vapour Pressure Regularities. II. W. Herz (*Zeitsch. Elektrochem.*, 1919, **25**, 45—46. Compare *ibid.*, 1918, **24**, 333).—The author has calculated the value of the constant c of the Ramsay and Young vapour pressure formula $\theta_1/\theta_2 = T_1/T_2 + c(\theta_1 - T_1)$ for chlorine, bromine, iodine, oxygen, sulphur, nitrogen, phosphorus, arsenic, bismuth, argon, krypton, xenon, copper, silver, zinc, cadmium, mercury, tin, and lead, and finds that the value is not constant in a single case. In the case of the non-metals there is an approximation to a constant, but in the case of the metals the divergence is sometimes so great that the sign changes. These constants depend in a high degree on the boiling points, and it seems likely that the inconstance may be due to inaccuracies in the determination of the boiling points. J. F. S.

Thermodynamics and Fractional Distillation. C. Mariller (*Bull. Assoc. Chim. Sucr. Dist.*, 1918, **35**, 45—51).—Chenard's assertion that the vapours produced on distilling mixtures of alcohol and water tend to separate into layers of different density (A., 1914, ii, 623; 1916, ii, 175) is refuted on theoretical and experimental grounds. Using apparatus similar to Chenard's, and guarding against external cooling, the author found no evidence of stratification. J. H. L.

Formula giving the Density of a Fluid in the Saturated State. E. Ariès (*Compt. rend.*, 1919, **168**, 714—717).—The formula deduced is $v_1 - v_2 = \Gamma(y_1 - y_2)RT_c/8P_c$, where v_1 is the volume of the molecular mass of the fluid entirely in the state of vapour, and v_2 entirely in the liquid state, these thus giving the densities in the two states of saturation. The author has tested this formula in the case of carbon dioxide, stannic chloride, methyl formate, and heptane, and finds that his calculated results agree closely with those observed by Young. W. G.

Reasons for the Movements of Camphor [on Water] and Allied Phenomena. J. Geppert (*Physikal. Zeitsch.*, 1919, **20**, 78—83).—A number of experiments are described showing that many substances, such as phenacetin, acetanilide, chloral hydrate, sulphonal, menthol, thymol, atropine sulphate, phthalic acid, and quinine, exhibit the same violent movements as camphor does on the surface of clean water. The rate of movement of oily substances, such as oleic acid, is also considered. The reasons for the movement are attributed to solution of the solid and also of the vapour, and the back pressure thereby occasioned. J. F. S.

Adsorption Compounds. II. R. Haller (*Kolloid Zeitsch.*, 1919, **24**, 56—66. Compare A., 1918, ii, 259).—A continuation of previous work on adsorption compounds; 0·5 gram of the dyes *m*-nitro-*p*-toluidine-red, *m*-nitroanisidine-red, *p*-nitro-*o*-anisidine-red, Sudan-G, Sudan-I, *p*-nitroaniline-red, alizarin-yellow G.G.W., fast-orange-O, brilliant orange, chromotrope 2R,

ponceau 2G, and *p*-nitrobenzeneazonaphtholsulphonic acid, dissolved in 50 c.c. of water, were treated with a 1% solution of brilliant-green as long as the latter was adsorbed. The adsorption products were isolated and characterised, and the colours produced when they were used to dye wool and cotton with tannic acid were noted. J. F. S.

Laws of the Capillary Rise in Porous Paper. Hans Schmidt (*Kolloid. Zeitsch.*, 1919, **24**, 49—56).—A number of experiments are described, designed to ascertain the connexion between the rise of an acid solution in filter paper and the extent to which a drop of the liquid spreads itself when allowed to fall on to a sheet of the same paper. It is shown that the amount of spreading is the same whether the porous paper is horizontal or vertical in the case of dilute solutions of hydrochloric acid.
J. F. S.

Retardation by Sugars of Diffusion of Acids in Gels. John Arthur Wilson (*J. Amer. Chem. Soc.*, 1919, **41**, 358—359).—A criticism of a paper by Graham and Graham (this vol., ii, 50). Compare Procter and Wilson (T., 1916, **109**, 307) and J. A. and H. W. Wilson (A., 1918, ii, 260). J. F. S.

Osmosis and Swelling of Disperse Systems. Wo. Ostwald and K. Mündler (*Kolloid. Zeitsch.*, 1919, **24**, 7—27).—A theoretical paper in which it is shown that the directly measured osmotic pressure of disperse systems is made up of two quantities: (i) the strict osmotic pressure, and (ii) an additional pressure, which is termed solvation, or swelling pressure. On the basis of this idea, a general solvation equation is established, $P_b = RT_{c_1} + kc_2^n$, in which P_b is the experimentally observed osmotic pressure, c_1 is the osmotic concentration, c_2 the swelling concentration, and k and n are constants. With dilute molecular or suspensoid dispersoids, the second factor of the equation disappears, and it passes over to the usual gas equation. On the other hand, in concentrated dispersoids, particularly in swelling gels, the osmotic concentration is very small, so that the first factor of the equation may be neglected. The expression $P_b = kc^n$ then, according to Posnjak and Freundlich, actually represents the dependence of the swelling pressure on the concentration in the case of gelatin and caoutchouc. The complete equation is applied to the osmotic measurements of solutions of sucrose, lævulose, and lactose of Morse, and Berkeley and Hartley, over the range $0{\cdot}1N$—$2{\cdot}0N$ and 0—80°. The agreement between the values calculated by the formula and the experimental values is excellent. In the case of sugar solutions, $n = 2$, so that as a first approximation the equation becomes $P_b = RT_{c_1} + kc_2^2$, but the value varies with the nature of the sugar and with the temperature. The osmotic pressure of very concentrated solutions of calcium ferrocyanide can be represented by the above equation to within 0·6%. In the case of con-

centrated sugar and calcium ferrocyanide solutions, the share of the total pressure due to the swelling pressure is very large. It increases, for example, with sucrose, with the concentration from 5% to 63% of the total pressure, and in the case of calcium ferrocyanide to 71%. It is also shown that the osmotic pressure of the hydrosols of iron, thorium hydroxide, and copper ferrocyanide follows the reduced solvation formula and also the swelling formula of Posnjak and Freundlich, a confirmation of the view that the taking up of water by such dispersoids is to be regarded more as the swelling of a liquid colloid than a simple osmotic process. The solvation formula does not hold for those systems in which internal changes in the state of aggregation occur with changes in concentration. The value of n lies always between 1·5 and 4·0, but most often it is found between 2 and 3. J. F. S.

Theory of Solubility. Albert Colson (*Compt. rend.*, 1919, **168**, 681—684. Compare A., 1916, ii, 475).—A theoretical discussion of certain points arising out of his formula

$$425L = T(V + \epsilon)idC/dT,$$

expressing all the particularities of solubility, where L is the heat of saturation, ϵ is the contraction of the final system, V is the volume of the solvent which saturates the dissolved molecule, C is the concentration or weight of anhydrous salt in 100 grams of a solution saturated at $T°$. W. G.

Electrical Synthesis of Colloids. The. Svedberg (*Kolloid. Zeitsch.*, 1919, **24**, 1—7).—Three processes are described by which highly disperse metal colloids may be produced. The author prefers to call these processes electrothermal colloid syntheses. A thin sheet of gold or silver is attached by gum arabic to a plate of glass which is immersed in ethyl alcohol. Two iron wires, attached to a 440-volt circuit and arranged to carry 10 amperes, are inserted in the liquid and brought into contact with the metal foil. Immediately, the metal round the iron poles is vaporised, and on condensation in the alcohol produces alco-sols. In the second process, narrow strips of gold, silver, zinc, and tin foil are attached to glass plates in the above-mentioned manner. The ends of the strips are thickened by a somewhat thicker piece of copper. Two iron wires, as before, are brought into contact with the copper, when the strip of foil between is entirely converted into the sol. In the third method, thin wires or strips of platinum, copper, lead, zinc, and aluminium are fastened to two thick iron wires immersed in alcohol, and a current passed, when the sols of these metals are produced. The process consists in the melting of the metal, which forms a number of small globules by capillary forces, and between which a number of small arcs are set up. This vaporises the metal, which condenses in the cooler regions to form highly disperse sols. The production of the sol depends more on the current strength than on the voltage employed. J. F. S.

Colours of Colloids. II. Wilder D. Bancroft (*J. Physical Chem.*, 1919, **23**, 1—35. Compare A., 1918, ii, 102).—A continuation of the discussion commenced in a previous paper (*loc. cit.*). The various colour effects produced by reflection and refraction of light are particularly considered in this communication.

J. F. S.

Colloid Chemistry of Indicators. II. Wolfgang Ostwald (*Kolloid. Zeitsch.*, 1919, **24**, 67—69. Compare A., 1912, ii, 439).—In a previous paper the author advanced the view that the colour change of indicators in many cases is a colloidal or disperse chemical process. The present paper is a résumé of the results of experiments on congo-rubin, which tend to substantiate the author's view. In aqueous solution, congo-rubin (sodium salt of benzidinebisazo-β-naphtholsulphonaphthionic acid) is a highly disperse system, intermediate between that of a typical colloid and a molecular disperse system. It is negatively charged and has a red colour, which is changed to blue by the addition of acids. This change is also brought about by the addition of a large number (seventy-five) of neutral salts, by alkaline salts, such as sodium carbonate, and by bases like barium hydroxide. On dilution, the blue solutions again become red; elevation of temperature, or the addition of alcohol, acetone, or pyridine, brings about the same reversal of colour change. By a further addition of an electrolyte to the blue solution, a precipitation of the colour substance is effected. The precipitate, on washing with water, passes into solution as a blue to violet hydrosol. It is stated that the blue solutions are less highly disperse than the red solutions, and on keeping a solution which has just turned blue, a slight precipitation occurs, which leaves a red solution. This solution may be turned blue by further addition of electrolyte. The red solutions contain a still more highly disperse orange-coloured fraction.

J. F. S.

Oscillation Method for Measuring the Size of Ultramicroscopic Particles. P. V. Wells and R. H. Gerke (*J. Amer. Chem. Soc.*, 1919, **41**, 312—329).—The diameter of the particles of gaseous dispersoids (in smoke) has been determined by an oscillation method. A quantity of the smoke is brought into the field of an ultramicroscope which lies in a rapidly alternating electrostatic field, and the path of the particles photographed. In this way the actual oscillations are obtained, and a measurement of the amplitude gives the distance travelled by the particle between two reversals of the current. Then, by Stokes's law, the motion of a particle in an electrostatic field is given by $Xe=3\pi\eta dv$, where X is the field in volts per cm., e the electronic charge (that is, $1{\cdot}59\times10^{-20}$), d the diameter in cm., η the viscosity of the medium, and v the velocity. It is shown that the diameter varies from 5×10^{-6} to 10^{-4}, and that the particles rapidly coalesce.

J. F. S.

Chemical Resistance. II. Applications of the Theory of Quanta to Chemical Dynamics. SHINKICHI HORIBA (*Mem. Coll. Sci. Kyoto Imp. Univ.*, 1918, **3**, 223—234. Compare A., 1916, ii, 305).—A mathematical paper in which, by an application of the theory of quanta, and on the hypothesis: "The reacting substances can only react when they are present in a certain elemental sphere of a reaction in a stoicheiometrical relation by their own kinetic energy, but the reaction will begin only when they are transformed into an active form by absorbing some energy from the surrounding medium," calculations of chemical resistance have been carried out. On this hypothesis of the mechanism of a chemical reaction, chemical resistance can easily be separated into two terms: (1) a term inversely proportional to the probability that the molecules of the reacting substances encounter in a stoicheiometrical relation in an elemental sphere by their own kinetic energy, and (2) a term proportional to the probability of the energy transport to reacting molecules from their surrounding medium. J. F. S.

Crystal Gratings and Bohr's Atom Model. M. BORN and A. LANDÉ (*Ber. deut. physikal. Ges.*, 1918, **20**, 202—209).—A mathematical paper in which the radius and number of electrons situated in the various rings of the metals of the alkalis and of the halogens are calculated. The elastic compressibility of the alkali haloids is calculated, and values obtained are about twice as large as the experimentally determined values. The absolute dimensions of the grating constant, δ, have been calculated, and the values indicate that the substances are twice as soft as the theory demands. J. F. S.

Calculation of the Compressibility of Regular Crystals from the Theory of the Grating. M. BORN and A. LANDÉ (*Ber. deut. physikal. Ges.*, 1918, **20**, 210—216. Compare preceding abstract).—The compressibility of the chloride, bromide, and iodide of sodium, potassium, and thallium has been calculated by means of the formula $x = 4{\cdot}26 \times 10^{-14}([\mu_+ + \mu_-]/\rho^3)$ on the basis that $n = 9$ and not 5, as was taken to be the case in the previous paper. The value of n has been calculated from the observed compressibilities, and a mean value 8·76 obtained. Using the value 9, a good agreement is found between the calculated and experimental values. In the case of calcium fluoride, to which the calculations were extended, $x = 1{\cdot}10 \times 10^{-12}$, whilst the experimental value is $1{\cdot}16 \times 10^{-12}$. J. F. S.

The Cubic Atom Model. M. BORN (*Ber. deut. physikal. Ges.*, 1918, **20**, 230—239).—The author, from a survey of the properties of the halogen derivatives of the alkalis, considers the cubic atom model is well founded, and whilst holding to the principles set down by Bohr, considers the matter mathematically with the object of bringing certain abnormalities into line with the general

theory. The question of the tetrahedral carbon atom is also considered. J. F. S.

Calculations of Ionic Charges in Crystals. J. WIMMER (*Physikal. Zeitsch.*, 1919, **20**, 92—93).—A theoretical paper in which it is shown that the ionic charges of diatomic crystals or crystals which can be regarded as made up of two equivalent atomic groups, and for which the grating structure is known, can be calculated by means of the formula $v/z=(G_1+G_2)/\sqrt{G_1G_2}$, in which v represents the valency, z the number of electrons, and G_1 and G_2 the atomic or molecular weights of the atoms or groups composing the molecule. The charges have been calculated for the crystals potassium chloride, sodium chloride, calcium fluoride, silica, calcium carbonate, potassium bromide, potassium iodide, sodium fluoride, lithium fluoride, and zinc sulphide. In the case of the first-named five substances, the value of the Drude constant k has been calculated. J. F. S.

The Theory of Duplex Affinity. SAMUEL HENRY CLIFFORD BRIGGS (T., 1919, **115**, 278—291).

Laboratory Apparatus for Rapid Evaporation. E. C. MERRILL and CLARE OLIN EWING (*J. Ind. Eng. Chem.*, 1919, **11**, 230).—Rapid evaporation of liquids is effected by passing a blast of heated air across the basins on the steam-bath. The air is forced through a brass cylinder containing cotton wool to act as a filter, and then through a copper coil, which is heated in the bath, and the outlet of which is connected with a series of blowers. Each of these is provided with a glass tap, and its height above the basin can be adjusted as desired. [See, further, *J. Soc. Chem. Ind.*, 1919, 268A.] C. A. M.

Theobald van Hogelande. F. M. JAEGER (*Chem. Weekblad*, 1919, **16**, 179—180).—The work "Merces Alchimistarum," Frankfurt-am-Mayn, 1610, attributed to Theobald van Hogelande (A., 1918, ii, 437), is shown to be a reprint of a German translation of his "De Alchimiæ Difficultatibus," Frankfurt, 1600.

W. S. M.

Inorganic Chemistry.

An Unusual Sulphur Crystal. F. RUSSELL BICHOWSKY (*J. Washington Acad. Sci.*, 1919, **9**, 126—131).—A crystallographic description is given of a well-developed crystal, D 2·01, of sulphur which was obtained accidentally by adding a hot alcoholic solution of ammonium polysulphide to a mixture of benzonitrile, hydroxylamine hydrochloride, and ether. L. J. S.

The Behaviour of Sulphur towards Carbonaceous Matter at High Temperatures. J. P. Wibaut (*Rec. trav. chim.*, 1919, **38**, 159—162).—When sugar, or the carbon obtained by charring it, or wood charcoal, is mixed with sulphur and the mixture heated in a closed crucible to a bright red incandescence, in each case a product is obtained which, after extraction first with carbon disulphide and then with ether, is found to contain sulphur to the extent of from 3—6%. Whether this sulphur is chemically combined or only absorbed is not decided. W. G.

Tellurium Sulphide. Aaron M. Hageman (*J. Amer. Chem. Soc.*, 1919, **41**, 329—341).—The introduction of hydrogen sulphide into an aqueous solution of tellurous acid at ordinary temperatures or below causes the immediate production of a reddish-brown precipitate, which is represented by the formula TeS_2. The production of this compound is independent of the acid concentration. At temperatures below $-20°$, tellurium sulphide is a stable compound, but at temperatures above $-20°$, dissociation takes place. At temperatures near $-20°$ this dissociation is slow, whilst at higher temperatures dissociation takes place more rapidly. The degree of dissociation at any time or temperature may be determined by the amount of sulphur which can be extracted by carbon disulphide. Dissociation never continues to completion. The dissociated mass extracted with carbon disulphide always retains at least 0·95% sulphur. This sulphur does not exist as a sulphide of tellurium which is decomposed by hydrochloric or hydrobromic acid of any strength, nor does it exist as a variety of sulphur insoluble in carbon disulphide. The compound TeS, often described, has no existence. The production of TeS_2 is independent of the medium in which the reaction is effected, for the action of hydrogen sulphide on solutions of tellurium tetrachloride in a large number of organic solvents gave exactly the same product. The dissociation and stability of tellurium sulphide is solely a question of temperature. Tellurium tetrachloride is found to be soluble in benzene, toluene, methyl alcohol, ethyl alcohol, *n*-butyl alcohol, amyl alcohol, benzyl alcohol, xylene, chloroform, and ethyl acetate, sparingly so in light petroleum, benzaldehyde, acetone, *iso*propyl bromide, and carbon tetrachloride, and insoluble in carbon disulphide. J. F. S.

Formation of Ammonia at High Temperatures. E. Briner (*Helv. Chim. Acta*, 1919, **2**, 162—166. Compare this vol., ii, 148).—A discussion of Maxted's recent work (T., 1918, **113**, 168, 386). In the first place, it is shown that the T^2 terms in Maxted's two formulæ have merely a corrective influence, and consequently they cannot be very significant in regions of temperature in which they have not been tested experimentally. This explains the great divergences between the values of K obtained from the two formulæ; at 1000° abs., up to which point both formulæ have been tested by experiment, there is agreement; at 2000°, the first

formula gives a value for K which is three times that derived from the second; at 3000°, the ratio is 10 to 1, and at 4000°, 100 to 1. Furthermore, assuming that at high temperatures the reaction is of the same nature as at lower temperatures, namely, one between molecules of nitrogen and hydrogen, these gases should unite completely at about 6000°, according to the first formula, and, in general, a gaseous mixture should become more and more complex with rise of temperature. This is contrary to the conclusions obtained by spectroscopic investigations, which clearly prove the elementary nature of the substances present in the hottest stars.

Such difficulties disappear if account is taken of the dissociation of the molecules into atoms (compare A., 1916, ii, 215). According to recent investigations, gases like hydrogen contain appreciable proportions of free atoms at much lower temperatures than was at one time supposed. The extra production of ammonia at high temperatures may be explained, therefore, by the greater kinetic energy of the free atoms of nitrogen and hydrogen. J. C. W.

Potassium Ammonosodiate, Potassium Ammonolithiate, Rubidium Ammonosodiate, and Ammonolithiate. Edward C. Franklin (*J. Physical Chem.*, 1919, **23**, 36—53).—A number of reactions between metallic amides in ammonia solution have been carried out, and as a result several ammono-salts have been isolated and characterised. These salts stand in the same relationship to ammonia as do the zincates, aluminates, and plumbites to water. A very complete list of the ammono-salts hitherto prepared is given. *Dipotassium ammonosodiate*, $NaNK_2,2NH_3$ or $NaNH_2,2KNH_2$ or $(Na[NH_2]_3)K_2$, is prepared (i) by the action of potassamide on sodamide in liquid ammonia solution, (ii) by the action of sodium iodide on an excess of potassamide in liquid ammonia, and (iii) by the action of sodium on potassamide in liquid ammonia in the presence of a small quantity of platinum black. This compound crystallises well, and does not lose ammonia at 100° in a vacuum; at higher temperatures it melts, loses ammonia, and attacks the containing glass vessel. *Monorubidium ammonosodiate*, $NaNHRb,NH_3$ or $NaNH_2,RbNH_2$ or $(Na[NH_2]_2)Rb$, is formed by the action of sodium and rubidium simultaneously on liquid ammonia. This compound is readily soluble in liquid ammonia, and is violently decomposed by water with the formation of the hydroxides of the metals. *Dirubidium ammonosodiate*, $NaNRb_2,2NH_3$ or $NaNH_2,2RbNH_2$ or $(Na[NH_2]_3)Rb_2$, is formed from the mother liquors of the previous compound by the addition of a large excess of rubidamide. This compound is considerably more soluble than the preceding compound in liquid ammonia. *Dipotassium ammonolithiate*, $LiNK_2,2NH_3$ or $LiNH_2,2KNH_2$ or $(Li[NH_2]_3)K_2$, is prepared by the action of potassamide on lithium iodide in liquid ammonia solution, and also by the action of lithium and potassium simultaneously on liquid

ammonia in the presence of platinum black. The salt forms minute, colourless crystals, which are practically insoluble in liquid ammonia. It is decomposed by acid amides and ammonium salts of oxygen and halogen acids (that is, by ammono-acids), with the formation of the corresponding salts of lithium, potassium, and ammonium. *Monorubidium ammonolithiate*, $LiNHRb,NH_3$ or $LiNH_2,RbNH_2$ or $(Li[NH_2]_2)Rb$, is prepared by the action of an excess of a solution of rubidamide in ammonia on metallic lithium in the presence of platinum black. A white, crystalline compound is obtained, which is sparingly soluble in liquid ammonia. It is decomposed by ammono-acids and by water, as in the preceding case. Attempts were made to separate rubidamide from potassamide by crystallisation from liquid ammonia, but without success, for these two substances form isomorphous mixtures which are relatively richer in rubidamide than the solution from which they separate. J. F. S.

Thermal Decomposition of certain Inorganic Trinitrides. E. Moles (*J. Chim. Phys.*, 1918, **16**, 401—404. Compare *ibid.*, 1917, **15**, 51).—A claim for priority over Hitch (compare A., 1918, ii, 398). W. G.

Method of Treating Beryl for the Extraction of Glucinum. H. Copaux (*Compt. rend.*, 1919, **168**, 610—612).—One part of powdered beryl is heated with two parts of sodium silicofluoride at 850° for thirty to forty minutes. At this temperature, the sodium silicofluoride decomposes, giving silicon fluoride, which attacks the beryl, giving glucinum fluoride and aluminium fluoride, which in turn combine with the sodium fluoride to give the corresponding double fluorides. The material is extracted with boiling water, in which the sodium glucinum fluoride dissolves, and the extract, after filtration, contains practically the whole of the glucinum in this form along with a little alumina and silica. A slight excess of boiling sodium hydroxide solution is added to the filtrate, and the precipitated oxides are collected and redissolved in sulphuric acid. The solution is concentrated, and the glucinum sulphate is allowed to crystallise out. By this method, 90% of the glucinum present in the mineral may be readily recovered.

On this process is based a method for the estimation of glucinum in beryl, using four parts of sodium silicofluoride to one part of beryl. The precipitation with sodium hydroxide is omitted, and an aliquot portion of the filtered aqueous extract is evaporated with an excess of sulphuric acid in a platinum dish until white fumes appear. The residue is dissolved in water, and an excess of ammonium hydroxide is added. The precipitate is filtered off, washed, dried, ignited, and weighed. Any silica in it is removed by means of hydrofluoric acid, and the aluminium and glucinum oxides are separated by Wunder and Weger's method (compare A., 1912, ii, 687). W. G.

Reaction between Sodium Chloride Solution and Metallic Magnesium. WILLIAM HUGHES (T., 1919, **115**, 272—277).

The Hammer-hardening of Lead, Tin and Thallium. PAUL NICOLARDOT (*Compt. rend.*, 1919, **168**, 558—560).—Lead, thallium, and tin all undergo hammer-hardening, but they anneal spontaneously at the ordinary temperature, the rate of annealing rising with rise in temperature. W. G.

The Extraction of Thallium from Pyrites Flue Dust. GEORGE SISSON and J. S. EDMONDSON (*J. Soc. Chem. Ind.*, 1919, **38**, 70T).—The dust collected from the flues situated between the pyrites kilns and the Glover tower of a sulphuric acid plant was found to contain 0·25% of thallium, representing about one part of thallium per million of pyrites burnt. The thallium was isolated by extracting the dust with dilute sulphuric acid and precipitating with hydrochloric acid. The crude thallium chloride was purified, dried, and reduced to metal by fusion with potassium cyanide and sodium carbonate, or, alternatively, with zinc. E. H. R.

Chemistry of Aluminium and Aluminium Alloys. JOHN G. A. RHODIN (*Trans. Faraday Soc.*, 1919, **14**, 134—149).—Experiments dealing with the working up of scrap aluminium are described. The specific gravity of aluminium containing various quantities of an equal mixture of copper and zinc has been determined, and it is shown that the density curve rises rapidly, but with decreasing rate, to 90% aluminium; between 90% and 80% aluminium, the curve is a slowly rising straight line which has an inflexion point somewhere about 76%. Aluminium is stated to dissolve alumina, and a method is devised for the estimation of the metallic aluminium apart from the alumina. A quantity of an aluminium alloy (2 grams) is placed in a tall beaker with 60 c.c. of 10% sodium hydroxide solution and heated on a sand-bath until the reaction becomes violent, after an induction period, when it is removed and cooled. The reaction is then completed by further heating on the sand-bath. The black residue is collected and dissolved in nitric acid (D 1·2). The two solutions thus obtained are analysed according to well-known methods. Comparison of the analytical results with the composition deduced from the specific gravity of the alloy showed a remarkably good agreement. By heating pure aluminium powder in air until the increase in weight corresponds with the formation of a compound Al_2O, a light grey, non-metallic powder is obtained. Boiling this powder with 10% sodium hydroxide dissolves a portion of it and leaves insoluble a light grey oxide, Al_3O_4. A number of determinations of the specific heat of aluminium alloys of copper and zinc are given. The following values were obtained: 98·6% aluminium, 0·2081; 90% aluminium, 10% copper, and 10% zinc, 0·1918; 80% aluminium, 20% zinc, 0·1844.

In the discussion on the paper, CLAUDE T. J. VAUTIN stated

that he had isolated the oxide Al_2O, a compound which produced a brilliant light under air oxidation. J. F. S.

The Formation of Troostite at Low Temperature in Carbon Steels and the Influence of the Temperature of Emersion in Interrupted Tempering. A. Portevin and Garvin (*Compt. rend.*, 1919, **168**, 731—733).—With velocities of tempering considerably higher than the critical velocities, by interrupting the tempering, very marked reheating may be observed, at temperatures down to 450°, and troostite is formed. The troostite is formed directly and immediately from the solid solution γ-iron–carbon at temperatures much lower than those at which it is formed by continuous tempering. With a velocity of tempering near to that of the critical velocity, it was possible to observe the formation of troostite at even lower temperatures (380°). If the velocity is inferior to the critical velocity, the reheating being produced at high temperatures during the period of rapid cooling, troostite is always obtained, and the temperature of emersion does not appreciably affect the structure and the hardness. With rapid tempering, it is possible, without appreciably altering the hardness, to stop the tempering at temperatures in the neighbourhood of 350°. W. G.

Structure of Iron-Carbon-Chromium Alloys. Takejirô Murakami (*Sci. Rep. Tohoku Imp. Univ.*, 1918, **7**, 217—276).—An investigation of the structure of 115 chromium–iron, chromium–carbon, and iron–carbon–chromium alloys. The influence of chromium on the magnetic critical point from A_2 was investigated, and it was found that it decreases at first slowly and then rapidly as the chromium content increases.

In the annealed alloys, the chromium carbide present is Cr_4C. At high temperatures, this decomposes into Cr_3C_2 and chromium. Three double carbides of iron and chromium were detected, namely, Fe_3C,Cr_4C, $(Fe_3C)_9,Cr_4C$, and $(Fe_3C)_{18},Cr_4C$. A portion of a thermal equilibrium diagram for the ternary system was drawn up. The binary system iron–chromium is a continuous series of solid solutions with a minimum about 70% of chromium. In the solid state, a certain undetermined solubility of the carbide Cr_4C in chromium occurs. Cr_4C and the double carbide $(Fe_3C)_9,Cr_4C$ form an uninterrupted series of solid solutions. The eutectic in the Cr_4C–Cr series occurs at about 1·8%. [See, further, *J. Soc. Chem. Ind.*, 1919, 257A.] F. C. Th.

The Reduction of Tungstic Oxide. C. W. Davis (*J. Ind. Eng. Chem.*, 1919, **11**, 201—204).—To obtain a satisfactory reduction of tungstic oxide to metallic tungsten, the material must be freed from water, which is best effected by a current of air at about 500°. On reducing the dried oxide with carbon, a blue or purple oxide is produced at 650° to 850°, a chocolate-brown mixture of oxides at 900° to 1050°, and metallic tungsten above 1050°.

The proportion of carbon required for the reduction ranges from 1:10 to 1·6:10, according to the temperature, time, and other conditions. Excess of carbon can be removed to a considerable extent by washing the product with water. When hydrogen is used as the reducing agent, the mixture of brown oxides is formed at 800° to 900°, whilst at 1080° a pure tungsten deposit (for example, 99·4%) is obtained. Reduction with gasoline vapour yields a product containing about 98% of tungsten with a considerable amount of carbon. [See, further, *J. Soc. Chem. Ind.*, 1919, 260A.] C. A. M.

The Partial Purification of Zirconium Oxide. A. J. PHILLIPS (*J. Amer. Ceram. Soc.*, 1918, **1**, 791—800).—Zirconia may be freed from iron oxide by mixing it with 4% of finely ground petroleum coke, making the mixture into balls, and heating them at 900° in a vertical cylindrical furnace (heated externally) through which a current of moist chlorine is passed. The reversible reaction $FeCl_3 \rightleftharpoons FeCl_2 + Cl$ constantly tends to form an equilibrium, which leaves some of the iron in the zirconia. If the rate of passage of the chlorine is increased beyond the requisite chlorine tension, chlorine is absorbed until the tension is reduced. With insufficient chlorine, the ferrous chloride is reduced. The water vapour present serves to produce hydrogen chloride, in which the ferrous chloride is readily volatile, whilst the zirconia is not affected. Hydrogen chloride without any free chlorine does not reduce the iron oxide below 0·5%. If the zirconia is heated by passing hot gases through it, the action of the chlorine is irregular and inefficient. Various methods of purification by fusing the zirconia with various salts proved unsatisfactory as far as the removal of the iron was concerned. [See *J. Soc. Chem. Ind.*, 1919, 252A.] A. B. S.

Mineralogical Chemistry.

Pyromorphite Group. M. AMADORI (*Gazzetta*, 1919, **49**, i, 38—102).—A summary and discussion of previous papers (A., 1913, ii, 216; 1915, ii, 358; 1918, ii, 365). T. H. P.

Non-identity of the Copper Silicates, Plancheite and Shattuckite. WALDEMAR T. SCHALLER (*J. Washington Acad. Sci.*, 1919, **9**, 131—134).—A reply to F. Zambonini (A., 1918, ii, 170). Although his new analysis of plancheite from the French Congo leads to nearly the same formula, $6CuO,5SiO_2,2H_2O$, as that for shattuckite ($2CuO,2SiO_2,H_2O$) from Arizona, the difference in the refractive indices is sufficient to prove that the two minerals are distinct. The highest value for plancheite ($\alpha=1·645$, $\gamma=1·715$) is less than the lowest value for shattuckite ($\alpha=1·752$, $\gamma=1·815$). L. J. S.

Analytical Chemistry.

A New Indicator for Bases and Acids. Marc Chauvierre (*Bull. Soc. chim.*, 1919, [iv], **25**, 118—119).—The reagent is prepared by boiling red beetroot with water and filtering the extract. It is a violet-red, opalescent solution, which is turned deep yellow with alkalis and retains its colour with acids. It is sensitive to both weak and strong inorganic and organic acids. Its colour is restored by sulphuric acid diluted to 1 in 10,000. Test papers cannot be prepared from it, as it does not fix on paper. W. G.

End-point in Oxidation Titrations determined by means of the Potentiometer. I. M. Kolthoff (*Chem. Weekblad*, 1919, **16**, 408—416).—When a reducing agent is titrated by means of an oxidising agent, the potential difference between the solution and an irreversible electrode immersed in it, measured against a normal electrode, varies in value during the titration, and in the neighbourhood of the end-point undergoes a rapid change. Expressions are deduced for the *E.M.F.* at the end-point and for the equilibrium constant of the reaction in terms of the normal potentials of the oxidising and the reducing agents. With the help of these, the sharpness of the end-point is discussed in relation to the magnitude of the equilibrium constant. W. S. M.

Arsenious Oxide as a Standard Substance in Iodometry. Robert M. Chapin (*J. Amer. Chem. Soc.*, 1919, **41**, 351—358).—Using weight burettes, solutions of highly purified arsenious oxide have been tested as to their trustworthiness as standards in place of iodine solutions. In six titrations of pure arsenious oxide against pure iodine, very precise results were obtained, the average of which agreed to within 1 in 3600 of the theoretical value. It is shown that arsenious oxide is a more trustworthy standard than iodine for volumetric work. Arsenious oxide is non-hygroscopic, and is permanent in both the solid state and in solution. The precautions necessary in the use of both arsenious oxide and iodine are discussed. J. F. S.

An Automatic Burette. George J. Hough (*J. Ind. Eng. Chem.*, 1919, **11**, 229).—The base of the burette consists of a glass tube with an outer jacket, which is passed through an opening in a rubber stopper made to fit into the mouth of the solution bottle. At the side of the jacket is a tube, to which can be attached a rubber pressure bulb, and it also has a side-tube intended to be closed with the finger when air is blown into the bottle. To equalise the pressure, a small hole is provided in the jacket above the level of the liquid in the bottle. When filled, the burette is

closed by a tap at the base, and the solution is drawn off through a side-tubulure ending in a tap. C. A. M.

Chlorine Absorption and Chlorination of Water. Abel Wolman and Linn H. Enslow (*J. Ind. Eng. Chem.*, 1919, **11**, 209—213).—A series of experiments on different waters to determine the velocity of absorption of available chlorine by the same water during varying intervals of time has shown that the velocity constant, K ($K = 1/t_2 - t_1 . \log N_1/N_2$), decreases, as a rule, with the time of contact. In the case of water containing little organic matter, however, it tends to become constant for different time intervals. The use of colour readings as an index of chlorine absorption is only trustworthy under known conditions with a given water, and the same conclusion applies to the measurement of the turbidity. The chlorine absorption does not increase in direct proportion with the increase in pollution (as measured by oxygen absorption), but shows a decreasing acceleration. The experiments cited appear to indicate that a thirty-minute absorption plus a high factor of safety is unnecessary, and that the addition of a small constant factor to the result, obtained by five minutes' absorption, would be as effective for the routine control of chlorination as the use of a longer time interval. [See also *J. Soc. Chem. Ind.*, 1919, 267A.] C. A. M.

Estimation of Halogens in Organic Compounds. D. Vorländer (*Ber.*, 1919, **52**, 308).—The Carius method is unnecessary, except, perhaps, for very volatile substances. The author uses a modification of Baubigny and Chavanne's process (A., 1903, ii, 510; 1904, ii, 203). In the absence of iodine, the substance (about 0·4 gram) is digested with a mixture of mercurous or mercuric nitrate (1 gram), potassium dichromate (6—8 grams), and pure sulphuric acid (40 c.c.) at 130—140°, and the halogen evolved is trapped by a sulphite solution and estimated by Volhard's method. If iodine is present, silver nitrate must be used, when iodic acid is formed.

[For sketch of original apparatus, see *J. Soc. Chem. Ind.*, 1904, 136.] J. C. W.

Apparatus for the Automatic Estimation of Small Amounts of Oxygen in Combustible Gas Mixtures or of Combustible Gases in Air. H. C. Greenwood and A. T. S. Zealley (*J. Soc. Chem. Ind.*, 1919, **38**, 87—90T).—The apparatus is designed for the purpose of detecting 0·1% or more of oxygen in gas mixtures, and of giving a continuous indication, not necessarily recorded, which will show at any moment the actual concentration. The principle involved is that of the combustion of the oxygen or other impurity by means of an intermittently heated platinum wire; automatic arrangements are provided for making and breaking the required electrical contacts, sealing up the combustion vessel during the heating period, cooling the gas, and

measuring the resulting contraction, ringing an electric bell at a specified oxygen concentration, and flushing out the spent gas by a new charge. A diagram is given of the apparatus, and the original paper should be consulted for details regarding its operation. W. P. S.

Reagent for, and Method of Estimating, Ozone. Louis Benoist (*Compt. rend.*, 1919, **168**, 612—615).—Fluorescein is a very sensitive reagent for the detection of ozone. At a dilution of 1 in 1,000,000, its solution loses its fluorescence in the presence of a trace of ozone, and is decolorised. At a dilution of 1 in 1000, it loses its fluorescence, but the solution remains yellow in colour. This phenomenon is not produced by oxygen, and it requires an enormous excess of nitrous vapours to destroy the fluorescence. Similarly, chlorine, even if present to the extent of three times the weight of fluorescein, and carbon dioxide, if present to the extent of twenty times the weight of fluorescein, do not destroy the fluorescence of a solution of fluorescein diluted to 1 in 1,000,000. Quantitative measurements indicate that the reaction takes place between two molecules of ozone and one molecule of fluorescein. An optical arrangement is described which permits of the detection of fluorescence in a solution diluted to 1 in 1,000,000,000, and thus, using 3 c.c. of such a solution, it is possible to detect and estimate 10^{-9} grams of ozone, which is a much smaller amount than can be detected by starch iodide. W. G.

Estimation of Sulphites and of Sulphur Dioxide in Gaseous Mixtures. Percy Haller (*J. Soc. Chem. Ind.*, 1919, **38**, 52—56T).—A trustworthy method for the estimation of sulphites consists in titration with potassium iodate solution strongly acidified with hydrochloric acid. The addition of glycerol (about 5% of the volume of the solution) to sulphite solutions or to sodium hydroxide solution used for absorbing sulphur dioxide prevents any loss due to oxidation of the sulphite by dissolved air, even when the solution is heated. The presence of the glycerol does not interfere with the subsequent titration of the sulphite; the results obtained for sulphur dioxide in gases are much higher than are found when the sulphur dioxide is absorbed in sodium hydroxide solution to which glycerol has not been added. W. P. S.

Estimation of Sulphates in the Presence of Iron. Hermann Koelsch (*Chem. Zeit.*, 1919, **43**, 117).—Examination of barium sulphate precipitates obtained in the estimation of sulphates in zinc blendes (compare A., 1916, ii, 194) showed that previous removal of iron had little effect on the purity of the barium sulphate as compared with precipitates obtained after the iron had been separated. The principal impurity in the barium sulphate precipitates, in both cases, was barium chloride; it amounted to about 7% of the weight of the precipitate. It is

pointed out that an error may be introduced owing to the reduction of a portion of the sulphate to sulphide during ignition unless care is taken to ensure oxidation. [See, further, *J. Soc. Chem. Ind.*, 1919, May.] W. P. S.

Estimation of Nitrates in Soil by the Phenoldisulphonic Acid Method. H. A. Noyes (*J. Ind. Eng. Chem.*, 1919, **11**, 213—218).—Extraction of the soil with cold water under specified conditions removes the whole of the nitrates present, and they may be accurately estimated by the phenoldisulphonic acid method in an aliquot portion of the filtrate. The presence of chlorides does not interfere with the estimation provided that the temperature is kept below that which causes the chlorides and nitrates to react with the dilute sulphuric acid. Organic substances which yield a coloured extract, or iron in the soil, may be removed by adding calcium hydroxide to the soil before the extraction with water. [See, further, *J. Soc. Chem. Ind.*, 1919, 265A.] C. A. M.

Estimation of Nitro-groups in Organic Compounds by means of Stannous Chloride. J. G. F. Druce (*Chem. News*, 1919, **118**, 133).—A modification of Young and Swain's method (A., 1898, ii, 186) for estimating nitro-groups by reduction with stannous chloride and titration of the excess of the latter with iodine solution is found to give satisfactory results (compare also Altmann, A., 1901, ii, 475). [See *J. Soc. Chem. Ind.*, 1919, 247A.] T. H. P.

Solvent Action of Dilute Citric and Nitric Acids on Rock Phosphate. J. A. Stenius (*J. Ind. Eng. Chem.*, 1919, **11**, 224—227).—The amount of phosphorus extracted from rock phosphate by citric acid of 0·2% strength was approximately the same as that extracted by neutral ammonium citrate solution. Variations in the strength of acid and in the amounts of rock phosphate treated had a great influence on the results. Calcium carbonate and other basic substances reduce the solvent action of citric acid, and the addition of the extra quantity of acid equivalent to the basic substance does not eliminate this influence. Extraction with dilute nitric acid (0·06 to 0·015%) removes still greater amounts of phosphorus, and this acid is therefore still less suitable than citric acid for estimating the available phosphorus. Although ammonium citrate solution does not extract all the available phosphorus, yet if used under uniform conditions it affords a test of the effect of any special treatment of rock phosphate. [See, further, *J. Soc. Chem. Ind.*, 1919, 265A.] C. A. M.

Methods of Glass Analysis, with Special Reference to Boric Acid and the Two Oxides of Arsenic. E. T. Allen and E. G. Zies (*J. Amer. Ceram. Soc.*, 1918, **1**, 739—786).—Tervalent and quinquevalent compounds of arsenic in glass may be separated

by heating the glass with hydrofluoric and sulphuric acids, which expel the tervalent arsenic, but leave the whole of the quinquevalent arsenic in the residue.

The quinquevalent arsenic may be estimated by precipitation as a sulphide, which is then oxidised to arsenic acid, reduced by hydriodic acid, and titrated with standard iodine solution, using starch as indicator. The total arsenic is estimated by fusing the glass with sodium carbonate and a little potassium nitrate, and determining the arsenic as just described. The nitre oxidises any arsenious compounds present, and so prevents their volatilisation. Boric acid is preferably estimated by Chapin's method, in which methyl alcohol and anhydrous calcium chloride are added to an acid solution of the fused glass, the methyl borate is distilled, and collected in sodium hydroxide solution. The methyl alcohol is removed from this by evaporation, the solution rendered acid with hydrochloric acid, heated to expel all carbon dioxide, then rendered neutral to *p*-nitrophenol by the addition of sodium hydroxide; mannitol is then added, and the free boric acid is titrated with standard sodium hydroxide. The results are affected by arsenious acid, but this can be avoided by oxidising the latter with hydrogen peroxide, as arsenic acid is inert. Relatively large amounts of fluorides affect the accuracy of the results, but the proportions usually present do not interfere. Special precautions required in the estimation of iron, zinc, lead, barium, and calcium by customary methods are described, and the suggestion is made that when analysing borosilicate glasses, the boric acid should be expelled by treating the residue obtained by evaporation (to separate the silica) with methyl alcohol before proceeding with the customary method of analysis. Attention is directed to the universal presence of hygroscopic moisture in finely powdered glass, and the effect of this on the analytical results. [For details, see *J. Soc. Chem. Ind.*, 1919, 254A.] A. B. S.

Instrument for the Estimation of Small Quantities of Carbon Monoxide in Hydrogen. E. K. RIDEAL and HUGH S. TAYLOR (*Analyst*, 1919, **44**, 89—94).—The method described depends on the preferential catalytic combustion of the carbon monoxide, the carbon dioxide formed being absorbed and estimated by measuring the conductivity of the solution. The gas (hydrogen) under examination enters the apparatus, and is measured by a gauge; it is then mixed with a small quantity of oxygen, obtained by the electrolysis of sodium hydroxide solution between nickel electrodes, and passes to a catalyst chamber. The latter contains a mixture of iron and chromium oxides, and also a small quantity of ceria and thoria, and is heated at 230°; the gases leaving the combustion chamber are passed through an absorption column, through which a current of *N*/200-calcium hydroxide solution flows at regulated speed, and the solution is collected in an electrolytic cell, where the conductivity is measured. [See, further, *J. Soc. Chem. Ind.*, 1919, 252A.] W. P. S.

[**Estimation of Glucinum in Beryl.**] H. Copaux (*Compt. rend.* 1919, **168**, 610—612).—See this vol., ii, 192.

The Products of the Reaction of Different Metals with Quinosol. N. Schoorl (*Pharm. Weekblad*, 1919, **56**, 325—328.)—Quinosol (the potassium salt of 8-hydroxyquinoline-5-sulphonic acid) gives an extremely delicate reaction with copper salts (Saul and Crawford, A., 1918, ii, 408). The author extends the use of this reagent, or of "superol (8-hydroxyquinoline sulphate), to the detection of arsenic (arsenate), barium, mercury (mercurous), lead, strontium, tin (stannous and stannic), iron (ferrous), and silver. The reagent superol is applied in the form of a 0·2% solution in water. The precipitates produced, except in the case of iron, are microcrystalline and of extremely characteristic appearance. 0·5 Mg. of copper per litre may be detected in this way.

W. S. M.

Estimation of Lead in Lead Salts. R. L. Morris (*Chem. and Drug.*, 1919, **91**, 52—54).—The method described in the British Pharmacopœia for the estimation of lead in lead salts (precipitation as oxalate and titration of the precipitate with permanganate solution) yields low results unless the precipitation is made in a solution containing at least 60% of acetic acid. [See, further, *J. Soc. Chem. Ind.*, 1919, 251A.] W. P. S.

Errors in the Analysis of Chrome Ironstone [Chromite], and a New Process. James Moir (*J. S. African Assoc. Anal. Chem.*, 1919, **2**, [i], 9—16).—From an investigation made with synthetic mixtures, it is concluded that errors amounting to 10% of the chromium present are quite possible in the analysis of chromite by the usual methods. A modification of the sodium peroxide fusion method is described by which results averaging 99·6% of the truth, with a total variation of about 1%, were obtained. [See, further, *J. Soc. Chem. Ind.*, 1919, 260A.]

W. E. F. P.

o-**Tolidine as a Colorimetric Test for Gold.** W. B. Pollard (*Analyst*, 1919, **44**, 94—95).—A 0·1% *o*-tolidine solution in 10% hydrochloric acid gives a bright yellow coloration with a gold chloride solution containing one part of gold in one million parts of water; the colour can just be detected in a solution containing one part in twenty millions if observed in a depth of 10 cm. of liquid. If free chlorine is present, the coloration requires about three minutes for full development. Ruthenium, iron, osmic acid, and vanadates also give a yellow coloration with the reagent, but other metals do not interfere with the test. In the presence of copper, a green coloration may be obtained instead of a pure yellow. Nitrites and other reducing substances must not be present. [See, further, *J. Soc. Chem. Ind.*, 1919, 269A.]

W. P. S.

The "Dracorubin" and "Dracorubin Capillary" Tests for Identifying and Differentiating Colourless Liquids. KARL DIETERICH (*Ber. Deut. pharm. Ges.*, 1918, **28**, 449—492).—The test papers employed are prepared by immersing strips of filter paper, 7 cm. long by 1 cm. wide, in an alcoholic or benzene solution of the portion of Sumatra palm resin (palm dragon's blood), which is insoluble in boiling light and heavy petroleum; the strips are dried before use. When these papers are immersed in various organic liquids, the red colouring matter is removed more or less completely, according to the solvent properties of the liquid. The rate of solution, the coloration of the liquid after fifteen minutes and twenty-four hours, respectively, and the appearance of the paper after removal from the liquid, are different in the case of such liquids as alcohol, ether, petroleum, benzene, acetone, turpentine, etc. In the "capillary" test, the paper is suspended so that its lower end dips to a depth of 1 cm. in the liquid. [See, further, *J. Soc. Chem. Ind.*, 1919, 306A.]

W. P. S.

Estimation of Glycerol by means of the Specific Gravity and Boiling Point. AD. GRÜN and TH. WIRTH (*Zeitsch. angew. Chem.*, 1919, **32**, i, 59—62).—According to various authorities, the specific gravity of pure glycerol varies by 0·0025 to 0·0030 for each 1% of water added, whilst the recorded values for pure glycerol itself vary up to 0·0110, which would correspond with about 3½% of water. The results obtained with samples of pure anhydrous glycerol by the authors were D_{15}^{15} 1·2653±0·0001, and were thus in agreement with those given by Gerlach (*Chem. Ind.*, **7**, 277), whose table must therefore be accepted as the most trustworthy. As was shown by Gerlach (*loc. cit.*), the boiling point of glycerol is lowered from 290° to 239° by the addition of 1% of water. In the determinations made by means of Schleiermacher's apparatus (A., 1891, 873), the boiling point of pure glycerol was found to be 283° to 284°, but this was proved to be due to the absorption of about 0·05% of water during the introduction of the glycerol into the capillary tube. The method affords the most trustworthy means of estimating small amounts of water in glycerol, and is applicable in the presence of organic and inorganic salts, such as sodium chloride, but cannot be used with crude glycerins containing polyglycerols. [See also *J. Soc. Chem. Ind.*, 1919, 295A.]

C. A. M.

Preparation of a Solution of Cupric Hydroxide in Sodium Hydroxide for the Detection and Estimation of Sugars. ED. JUSTIN-MUELLER (*J. Pharm. Chim.*, 1919, [vii], **19**, 18—20).—A solution, which serves all the purposes of Fehling's solution, may be obtained by adding 20 c.c. of 10% copper sulphate solution to 100 c.c. of 33·69% sodium hydroxide solution; the solution remains clear when kept, and does not give a precipitate when heated.

W. P. S.

Analysis of Cows' Milk, Particularly the Estimation of Lactose. Hans Salomon and Rudolf Diehl (*Ber. Deut. pharm. Ges.*, 1918, **28**, 493—498).—Analyses are recorded showing that the quality of cows' milk has not been affected by the poor fodder available lately in Germany. In the estimation of lactose, the preliminary removal of proteins, etc., by precipitation with copper sulphate and sodium hydroxide, is not always complete, especially in the case of milks which have been preserved by the addition of formaldehyde; the use of zinc sulphate, copper sulphate alone, or a mixture of asaprol (sodium β-naphthol-α-monosulphonate) and citric acid is recommended for the purpose. W. P. S.

A New Method for the Estimation of Oxalic Acid. Hugo Krause (*Ber.*, 1919, **52**, [*B*], 426—432).—When oxalic acid is heated with acetic anhydride at 100°, it decomposes briskly and quantitatively into carbon monoxide and carbon dioxide. Performed in a tube fitted with a generator of carbon dioxide and a nitrometer filled with potassium hydroxide, the reaction may therefore be used for quantitative purposes. The only common organic acid which also gives carbon monoxide under these conditions is formic acid, although even this reacts more sluggishly.

For soluble oxalates, the material is first evaporated with an excess of hydrochloric acid, and the slightly moist residue is spread out on the walls of the tube by shaking during the evaporation. Insoluble oxalates are treated with a mixture of acetic anhydride and sulphuric acid (9:1), but the method is not so good in this case, as the mixture alone develops some insoluble gas, necessitating a "blank" experiment, nor is it specific for oxalic acid.

J. C. W.

Volumetric Method for the Estimation of Salicylic Acid in the Presence of Salicylaldehyde. R. Berg (*Chem. Zeit.*, 1919, **43**, 129).—The method depends on the formation of a yellow coloration when a solution of salicylaldehyde is treated with a slight excess of free alkali; the aldehyde thus acts as an indicator. An ethereal solution containing salicylic acid and salicylaldehyde is extracted with several successive quantities of $N/20$-sodium hydrogen carbonate solution, and the aqueous extract is titrated with $N/20$-sulphuric acid, the solution being boiled after each addition of the acid to expel carbon dioxide. The end-point is denoted by the solution remaining colourless when boiled. [See, further, *J. Soc. Chem. Ind.*, 1919, May.] W. P. S.

Volumetric Method for the Estimation of Urea. Applicable to Urine, Blood, Serum, etc. Golse (*Bull. Soc. Pharm. Bordeaux*, 1918, **56**, 188; from *J. Pharm. Chim.*, 1919, [vii], **19**, 20—22).—The urea solution is treated with a definite quantity (an excess) of sodium hypobromite solution, and, after one minute, potassium iodide and acetic acid are added and the liberated iodine is titrated with thiosulphate solution. The same

volume of hypobromite solution is then treated separately with potassium iodide and acetic acid, and titrated. The difference between the two titrations is equivalent to the amount of urea present; 6 atoms of iodine correspond with 1 molecule of urea. In the case of urine, the urea is precipitated as a mercury compound by treating the urine with Patein's reagent and sodium hydroxide; the precipitate is collected, washed, dissolved in acetic acid, and the solution treated as described. Blood is clarified with trichloroacetic acid, filtered, the urea precipitated in the filtrate by means of Patein's reagent and sodium hydroxide, and the process continued as above. W. P. S.

Reduction of the Quantity of Humin Nitrogen Formed in the Hydrolysis of the Nitrogenous Constituents of Feeding-stuffs. H. C. Eckstein and H. S. Grindley (*J. Biol. Chem.*, 1919, **37**, 373—376. Compare A., 1915, ii, 598, and A., 1916, i, 623; ii, 119).—The authors have attempted to render the Van Slyke method for the determination of the chemical groups characteristic of the amino-acids of proteins applicable with greater accuracy than heretofore in the analysis of feeding stuffs. In the first place, the interference of some of the non-protein nitrogenous constituents, such as certain lipoids, pigments, betaines, amygdalin, alkaloids, and some amides has been obviated by completely extracting the food product first with ether and then with cold absolute alcohol. In the second place, a method has been perfected by which the percentages of the humin nitrogen formed in the hydrolysis of the nitrogenous constituents of feeding stuffs are reduced so that they compare favourably with those obtained for pure proteins. This is effected, firstly, by the extraction referred to above, after which insoluble carbohydrates are converted as far as possible into soluble carbohydrates by boiling with 0·1% hydrochloric acid. The greater part of the soluble proteins is separated before hydrolysis from the soluble carbohydrates by neutralising the mineral acid and precipitating with alcohol. The small portion of proteins remaining in solution is hydrolysed by boiling with 5% hydrochloric acid instead of 20%.

By this method, the humin nitrogen is represented by values approximately a third of those obtained by the direct method. J. C. D.

The Indophenine Reaction. Edward Wray (*J. Soc. Chem. Ind.*, 1919, **38**, 83—84T. Compare A., 1904, i, 337; 1905, ii, 779).—A green coloration instead of blue is obtained in this reaction unless a small quantity of an oxidising substance, preferably nitric acid, is present. The test is made as follows: 25 c.c. of a 0·05% isatin solution in pure sulphuric acid are placed in a stoppered cylinder, and 1 c.c. of the benzene to be tested for thiophen is added, followed by 25 c.c. of sulphuric acid containing one drop of nitric acid; a blue coloration appears when the mixture is shaken. W. P. S.

General and Physical Chemistry.

Relation between Intensity of Tyndall Beam and Size of Particles. Richard C. Tolman, Roscoe H. Gerke, Adin P. Brooks, Albert G. Herman, Robert S. Mulliken, and Harry De W. Smyth (*J. Amer. Chem. Soc.*, 1919, **41**, 575—587).—The intensity of the Tyndall beam in rosin smokes has been investigated further by the method previously described (this vol., ii, 180). In the case of smoke, since the particles are not of uniform size, no attempt was made to measure the size of the particles, but the results show that for the range of particles 10^{-6}—10^{-4} cm., the Tyndall-meter reading increases with increased dispersion. Suspensions of silica particles in water were prepared, and the intensity of the Tyndall beam in these suspensions investigated. The particles were of uniform size and varied in the different suspensions from 10—260×10^{-5} cm. The Tyndall-meter readings in the case of silica suspensions increase with decreasing diameter of the particles. The results show that the readings are closely proportional to the reciprocal of the diameter of the particles. The relationships between the readings (T) and size of the particles are given by the equations $T = knd^6$ for very small particles and $T = k^1nd^2$ for large particles; d is the diameter of the particles, n the number of particles per c.c., and k and k^1 are constants. When the total concentration of the suspensions is given by c; $c \propto nd^3$, hence the equations may be written $T = kcd^3$ and $T = k^1c/d$. J. F. S.

Absorption by Troubled Media. Application to the Estimation of Suspensions. Charles Chéneveau and René Audubert (*Compt. rend.*, 1919, **168**, 766—768).—The authors deduce the formula $1 - I/I_0 = e^{-B/M^\beta}$, where I/I_0 is the coefficient of transmission of light of the fine suspension, M is the total mass of particles, and B and β are two constants dependent only on the nature of the particles in suspension and the wave-length of light used. The accuracy of this formula has been verified for certain heterogeneous suspensions of mastic and for suspensions of silver chloride and barium sulphate. This thus provides a method of determining the amount of material in suspension providing there is no immediate sedimentation. W. G.

Conductivity and Absorption of Sodium Vapour. Adolfo Campetti (*Nuovo Cim.*, 1918, [vi], **16**, ii, 115—138).—The results of the author's experiments show that, in unsaturated sodium vapour kept in the dark and freed from electrons emitted from the surface of the fused metal, spontaneous ionisation in the volume of the vapour occurs at high temperature; this ionisation becomes clearly manifest above 400° without marked dissymmetry as regards

the sign of the disperse charge. Such conductivity in the volume of the vapour is closely connected with the commencement of the absorption of the *D*-line, which under the above conditions is observed only at about 430°, but then persists when the temperature falls considerably. The cause of the appearance of absorption at somewhat lower temperatures under the ordinary conditions of observation is clearly shown to be the presence of electrons either given off from the surface of the molten metal or arising from the atoms of the metal in the state of vapour as a result of photo-electric action. It appears probable that the emitting or absorbing vibrators in sodium vapour are, for the *D*-line, the positive atom ions. T. H. P.

Spectrum of Neon. K. W. Meissner (*Ann. Physik*, 1919, [iv], **58**, 333—374).—The red and infra-red spectrum of neon has been investigated by the interferometric method of Fabry and Perot (*Ann. Chim. Phys.*, 1897, [vii], **12**, 459), and also by means of a concave grating of 1 metre radius. Some seventy-five lines are recorded between the wave-lengths 7051·314 and 9840·42 A.U., and in all cases the vacuum wave-length is calculated. The wave-lengths of the present measurements, together with those of previous measurements of the other portions of the spectrum, are examined with the object of arranging them in series, and the relationships of the eight series groups calculated. J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. Deslandres (*Compt. rend.*, 1919, **168**, 861—868).—Vegard's work (compare A., 1918, ii, 93, 94, 144) gives data concerning the inner rings of electrons adjacent to the nucleus, and the author considers that a study of band spectra may throw some light on the composition of the outer rings. The edges of the bands, which form the structure of the spectra, are given by $\nu = B(n+\beta)^2/2 - C(p+\gamma)^2/2 + K$, where B, C, K, β, and γ are constants, n and p being successive whole numbers.

The three types of spectra, line, band, and *X*-ray, are due to the action, more or less strong, of ions and electrons which encounter the atom. If the electron which arrives is very rapid, it penetrates to the nucleus and disarranges the ring nearest to the nucleus, causing it to lose an electron and giving rise to *X*-rays. If the electron is less rapid, only an outer ring is disarranged, and the line spectrum results. If, however, the velocity of the approaching electron is still less, the atom is only deformed and emits the band spectrum. W. G.

The Verification of Bohr's Atomic Theory of Optical Spectra by Investigations of the Non-elastic Collisions of Slow Electrons with Gas Molecules. J. Franck and G. Hertz (*Physikal. Zeitsch.*, 1919, **20**, 132—143. Compare *ibid.*, A., 1914, ii, 515; 1916, ii, 461).—The principle that for the monatomic gases without affinity for electrons the electrons are reflected from the

atoms with perfect elasticity up to a critical velocity of collision, when they lose their total energy of translation and give rise to radiation, has been found to be in complete accord with Bohr's theory. The critical energy of the electron in the case of mercury vapour, derived from a potential difference of $4{\cdot}9 \pm 0{\cdot}1$ volt, is equal to $h\nu$, where h is the quantum and ν the frequency corresponding with 2536 Å. in the ultra-violet spectrum of mercury. The absorption and emission lines can be excited by free electrons, which suffer a loss of energy of $h\nu$ on collision. For normal, not excited, atoms, the change of the electron from one steady orbit to another corresponds with the absorption spectrum series. The limit of frequency of the series in the ultra-violet multiplied by the quantum h gives the work done in ionising the atom, and the limit may be calculated from the ionising potential and vice versâ. The investigation of inelastic electronic collision and its attendant light emission gives a new means of analysing the lines of a spectrum into series and determining their relation. F. S.

Explanation of the Röntgen Spectrum and the Constitution of the Atom. L. Vegard (*Physikal. Zeitsch.*, 1919, **20**, 97—104).—A theoretical paper in which the main results of previous publications are summarised (A., 1918, ii, 93, 94, 144). A generalised frequency formula is developed on the basis of the preceding work, and this is tested by comparison of curves produced from results calculated by this formula with the corresponding experimental curves. J. F. S.

***X*-Ray Spectroscopy. The *L*-Absorption Spectrum of Radium.** M. de Broglie (*Compt. rend.*, 1919, **168**, 854—855).—The *L*-absorption band of radium has been obtained by passing a beam of *X*-rays through a glass capillary tube containing solid radium sulphate. The tube is fixed before the spectroscope slit. The wave-length $\lambda = 0{\cdot}659 \times 10^{-8}$ cm. is found for this band, and calculations from this value lead to 88 as the atomic number of radium. J. F. S.

Crystalline Structure of Alums and the Rôle of Water of Crystallisation. L. Vegard (*Ann. Physik*, 1919, [iv], **58**, 291—296).—Polemical against Schaefer and Schubert (A., 1916, ii, 505). The author shows that the measurements of Schaefer and Schubert do not prove that water of crystallisation occurs as a structural component in the grating system, and that the claim for priority made by these authors is unfounded. J. F. S.

Optical Investigation of the Constitution of some Oxygen Acids of Chlorine and Bromine and of their Esters and Salts. Konrad Schaefer and Willy Köhler (*Zeitsch. physikal Chem.*, 1919, **93**, 312—324).—The absorption spectra of a number of the oxygen acids of the halogens, their esters, and salts have been measured. In the case of hypochlorous acid, ethyl hypo-

chlorite, and several metallic hypochlorites it is shown that the acid and ester have identical absorption spectra, but when the acid is completely neutralised by sodium hydroxide, the absorption spectrum changes in the sense that a deep, well-defined, broad band appears. Incomplete neutralisation gives an absorption spectrum which indicates both acid and salt. The author puts forward the formula Cl·OH and Cl·OEt for the acid and ester respectively, and $\overset{\text{Cl}}{\underset{\text{O}}{|}}\!>\!\text{Na} \rightleftharpoons \overset{\text{Cl}}{\underset{\text{O}}{|}}\!>\!^{-} + \text{Na}^{+}$ for the salt. Hypobromous acid and sodium hypobromite give absorption spectra similar to those of the corresponding chlorine compounds. Solutions of chlorine dioxide, chlorous acid, and several chlorites were also examined. Gaseous chlorine dioxide shows a broad band and a large number of narrow bands, whilst on solution the bands are broadened and many run together, but in general the region of absorption remains the same. The maximum of absorption is at 2900, and the minimum at the frequency 3800. These results indicate that there is little formation of chloric or chlorous acid on solution. On neutralisation, the band disappears, so that the chlorites have a different constitution from the acid, the formulæ $\text{O}=\text{Cl}\cdot\text{OH}$ and $\text{Cl}\overset{\text{O}}{\underset{\text{O}}{|}}\!>\!\text{M}$ being suggested in the two cases. Bromic acid, iodic acid, and their alkali salts were also investigated. The only difference observed in these cases was the shifting of the terminal absorption toward higher frequencies in the case of the bromine compounds. The measurements show that the constitution of these acids is probably that of a true acid, as distinguished from a pseudo-acid. J. F. S.

Use of Einstein's Photochemical Equivalent Law. I. W. Nernst (*Zeitsch. Elektrochem.*, 1918, **24**, 335—336).—A theoretical paper in which the reason for the inapplicability of the Einstein photochemical law to the photosynthesis of hydrogen chloride is put forward. The primary action of light is the splitting of the chlorine molecule, this then reacts $\text{Cl}+\text{H}_2=\text{HCl}+\text{H}+25{,}000$ cal., and the hydrogen atom thus produced reacts with a chlorine molecule, $\text{H}+\text{Cl}_2=\text{HCl}+\text{Cl}+19{,}000$ cal. This explains why so much more hydrogen chloride is produced than corresponds with the requirement of the Einstein law. This also explains the negative catalytic effect of impurities on this reaction. The chlorine and hydrogen atoms are very reactive substances, and consequently will be removed from the reaction system by their combination with the impurities. This view is confirmed by the limited reaction when bromine vapour and hydrogen are illuminated, for, as the equation $\text{Br}+\text{H}_2=\text{HBr}+\text{H}-15{,}000$ cal. shows, hydrogen is not a suitable acceptor for bromine.

J. F. S.

Use of Einstein's Photochemical Equivalent Law. II. Lotte Pusch (*Zeitsch. Elektrochem.*, 1918, **24**, 336—339. Compare preceding abstract).—The reaction between bromine vapour

and hydrogen in the presence of toluene, hexane, and heptane when exposed to light has been investigated. The results confirm the view put forward in the preceding paper that in the case of chlorine and hydrogen the primary reaction is strictly in accordance with the Einstein law, and that the secondary reactions account for the extremely large quantities of hydrogen chloride produced. J. F. S.

The Possibility of Separating Isotopes. F. A. Lindemann and F. W. Aston (*Phil. Mag.*, 1919, [vi], **37**, 523—534).—The possible methods of separating isotopes, distillation, to which, thermodynamically, chemical separation is closely allied, diffusion, density, and positive rays, are discussed theoretically. The conclusion is reached that separation by distillation and chemical methods ought to be possible under appropriate conditions, although the separation may be small. None of the possible physical methods holds out any prospect of effecting an easy separation, centrifugal separation being the most promising. For neon and meta-neon, with a peripheral velocity of 10^5 cm. per second, it is calculated that the apparent atomic weight of the gas at the edge should be 1·0065 times that of the gas at the centre, and for thorio- and uranio-lead a nearly 50% increase in the concentration of the former at the edge might result.

Experiments are described on the fractionation of atmospheric neon by charcoal at liquid air temperature. After about 3000 fractionations, in which the gas was divided into seven main fractions, the density as determined by the quartz micro-balance was unchanged. F. S.

Protactinium and the Life Period of Actinium. Otto Hahn and Lise Meitner (*Physikal. Zeitsch.*, 1919, **20**, 127—130. Compare *ibid.*, A., 1918, ii, 345; Soddy and Cranston, A., 1918, ii, 211).—Evidence of the period of actinium obtained from the proportionate increase of the α-radiation of protactinium preparations with time confirms the value obtained directly from the rate of decay of the radiation of actinium preparations. From the known ranges of the six α-rays involved in the protactinium–actinium series, the ratio of the initial ionisation produced by a thin film of protactinium to that when the actinium and its products are in equilibrium with the protactinium is calculated to be 1:5·74. From the proportionate increase of α-radiation of five preparations over periods from 400 to 600 days, a half-period of actinium of twenty years is deduced. This indicates that in the carbon tetrachloride sublimation of Soddy and Cranston less than 1% of the eka-tantalum (protactinium) in the mineral was separated. The value found from the decay curve of the radiation of actinium over seven years gives for the half-period of actinium twenty years (±10%). This corresponds with a period of average life of 28·8 years. F. S.

Chemical Action produced by Radium Emanation. I. Combination of Hydrogen and Oxygen. S. C. Lind (*J. Amer. Chem. Soc.*, 1919, **41**, 531—551).—The velocity of combination of hydrogen and oxygen under the influence of radium emanation has been investigated. The experiments were effected in spherical and cylindrical bulbs of varying size by a method which is a slight modification of that of Cameron and Ramsay (T., 1908, **93**, 966—992). It is shown that the velocity of reaction in a given volume is dependent on two variables only, the quantity of emanation, E, and the gas pressure, P. The velocity constant obtained by integration of the equation arising from this assumption has been verified. It has the form $(\log P/P_0)/E_0(e^{-\lambda t}-1)=\text{const.}$ The effect of increasing the spherical volume is to diminish the velocity constant (expressed in terms of pressure) according to the equation $84{\cdot}1/D^2=\text{const.}$, where D is the diameter in cm. This is to be expected from the increase of the average path of the α-particle proportional to D, whilst the pressure effect diminishes proportionally to D^3. The above formula is applicable only to globes in which the size of the shortest α-ray is not exceeded by the diameter. Varying proportions of hydrogen and oxygen change the velocity in the way which is to be expected from the change produced in the specific ionisations. Excess of oxygen gives a velocity higher than normal, which increases as the proportion of oxygen increases. Excess of hydrogen produces the opposite effect. The temperature-coefficient of the reaction between 0° and 25° is zero, as would be expected from ionisation. Calculation of the ionisation by the method of average path of the α-particles shows that for each pair of ions produced in the gaseous mixture, 3·9 molecules of water are formed: this value agrees fairly well with 3·7 found by Scheuer (A., 1914, ii, 762). The reaction in cylindrical volumes obeys the same laws as that in spherical volumes, which would appear to confirm the author's original contention that the average path in a cylinder is the same as in a sphere of equal volume (*Amer. Electrochem. Trans.*, **34**). J. F. S.

Chemical Action produced by Radium Emanation. II. Chemical Effect of Recoil Atoms. S. C. Lind (*J. Amer. Chem. Soc.*, 1919, **41**, 551—559. See preceding abstract).—The action of radium emanation in causing the combination of electrolytic hydrogen and oxygen is abnormally high in small spheres, particularly at low gaseous pressures. The action is shown to be six to seven times greater than that due to the normal α-ray effect. This abnormally high velocity is explained by the assumption that the recoil atoms contribute to the reaction in proportion to their relative ionising power. The results of the author's calculations and experiments are in general agreement with Wertenstein's ionisation data for recoil atoms (A., 1914, ii, 514). J. F. S.

Determination of the Ionisation Potential for Electrons in Helium. Frank Horton and Ann Catherine Davies (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 408—429).—The ionisation potential of

electrons generated by a heated tantalum wire in helium of low pressure has been experimentally determined. The experiments show that radiation occurs when electrons having a velocity of about 20·5 volts collide with helium atoms, and that this is not accompanied by any ionisation of the gas. It is also shown that ionisation of the helium occurs when the velocity of the electrons is raised to about 25·7 volts, and that no other type of radiation is produced at this point. The potential values were obtained from an accurate investigation of the position of the bends of the current–potential difference curves over a range of 2—3 volts in the neighbourhood of the value. The mean values from these experiments were 20·4 volts and 25·7 volts respectively. By a method in which the value of V_3 was made zero, and the electrons could produce radiation or ionisation over longer paths, the mean values 20·45 volts and 25·5 volts were obtained. It may be taken that 20·4 volts represents the minimum radiation potential and 25·6 volts the minimum ionisation potential. These values confirm Bohr's suggestion that radiation, and not ionisation, occurs at about 20 volts, but the value found for the ionisation potential is considerably lower than the value, 29 volts, deduced from Bohr's theory of the structure of the helium atom. J. F. S.

Molecular Electric Field in Gases. P. Debye (*Physikal. Zeitsch.*, 1919, **20**, 160—161).—A theoretical paper in which calculations, based on the Stark hypothesis that the broadening of spectral lines is to be attributed to a molecular electric field, are made by which the approximate dimensions of the molecular electric field are calculated. Assuming that the charge of an electron is 5×10^{-10} g.$^{\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-1}$ (electrostatic units), and the radius of the molecule is 10^{-8} cm., it is shown that the charge on a charged molecule or ion may be taken as 5×10^{-10} g.$^{\frac{1}{2}}$ cm.$^{\frac{3}{2}}$ sec.$^{-1}$, and in the case of an uncharged molecule which bears an electric moment, this may be put at 5×10^{-18} g.$^{\frac{1}{2}}$ cm.$^{\frac{5}{2}}$ sec.$^{-1}$. If the electric moment disappears, the electric moment of inertia is then calculated to 5×10^{-26} g.$^{\frac{1}{2}}$ cm.$^{\frac{7}{2}}$ sec.$^{-1}$. Values of the above dimensions have been recently obtained by Jona (this vol., ii, 130). The value of the field strength due to the ions (F_1) is given by $F_1 = en^{\frac{2}{3}}$, where e is the ionic charge and n the number of gas molecules per cubic centimetre. The field strength, F_2, due to uncharged molecules which have an electric moment, is given by $F_2 = mn$, where m is the electric moment, and for the case where the electric moment is zero and only an electric moment of inertia present. $F_3 = \Theta\, n^{\frac{4}{3}}$ gives the field due to this cause, where Θ is the electric moment of inertia. Substituting the appropriate data $F_1 = 4500$ electrostatic units $= 1{,}350{,}000$ volts/cm., $F_2 = 135$ electrostatic units $= 40.500$ volts/cm., and $F_3 = 4$ electrostatic units $=$ 1200 volts/cm. In the case of ammonia and sulphur dioxide, the electric moment is actually of the above order, and an electric field of 4×10^4 volts/cm. is existent. J. F. S.

Electromotive Activity of Carbon Monoxide. FRIEDRICH AUERBACH (*Zeitsch. Elektrochem.*, 1919, **25**, 82—84).—A theoretical paper in which the activity of carbon monoxide in electromotive processes is considered. It is shown that the *E.M.F.* given by Hofmann (this vol., ii, 8) for the element O_2/CO may not be directly compared with that calculated from the free energy of the reaction $2CO + O_2 \rightleftharpoons 2CO_2$, because in alkaline electrolytes carbon monoxide is not burnt to carbon dioxide, but to carbonate. In the present calculations, the *E.M.F.* is much smaller than that observed by Hofmann. J. F. S.

A Modified Hydrogen Electrode. J. HUDIG and W. STURM (*Chem. Weekblad*, 1919, **16**, 473—481).—In their measurements of the hydrogen-ion concentration of aqueous soil extracts by means of the hydrogen electrode, the authors experienced difficulty in obtaining constant results for any one extract, even after filtration of the latter through an ultra-filter. Whilst no explanation of the observed fluctuations in *E.M.F.* is suggested, it is found possible to obtain satisfactory constancy in the readings by the following modifications in the construction and use of the hydrogen electrode. The electrode consists of a platinum gauze cylinder platinised over a gold coating. The soil suspension is contained in a closed vessel, through the stopper of which pass the electrode, gas inlet and outlet tubes, electrolyte tube, and a stirring gear motor driven through a mercury seal. A rapid stream of hydrogen is supplied both to the inner and to the outer surface of the gauze cylinder during the measurement, whilst soil and liquid are kept in intimate contact by vigorous stirring. W. S. M.

The Theory of Electrolytic Ions. IX. Space-filling and Mobility of Univalent Organic Ions. R. LORENZ (*Zeitsch. anorg. Chem.*, 1919, **105**, 175—186).—The author has calculated the space-filling numbers of more than one hundred univalent organic cations, containing from 6 to 44 atoms (compare A., 1918, ii, 303). The space-filling number ψ is the ratio of two volumes, ϕ/V, where ϕ is the ionic volume calculated from the ionic mobility and V is the volume derived from the density or from Kopp's formula. The ion radius, r, is given by the formula $r = 1/u \times 8{\cdot}954{\cdot}10^{-7}$. In the series of ions examined, this radius is found to be a linear function of the number of atoms in the ion. Hevesy (A., 1916, ii, 594) has advanced the theory that the ions in solution endeavour to attain an approximately constant potential, which, in the case of water, is about 70 millivolts. The normal radius of an ion charged to this potential he calculates to be $2{\cdot}8 \times 10^{-8}$ cm. To adjust their potential, the smaller ions, he supposes, increase their radius by becoming hydrated, thereby lowering their mobility. In the series of ions under examination, this "normal" radius, corresponding with a "normal" mobility, is reached with not fewer than 27 atoms in the ion. According to Hevesy's theory, ions with fewer than 27 atoms should become

hydrated to bring their radii and mobilities to the "normal" value. There is no evidence that they do become so hydrated, however, for the relation between the number of atoms and the ionic radius is linear, and there is no discontinuity in the curve at about 27 atoms. Further, there is very little difference between the mean values of the space-filling numbers with more than 27 atoms ($\psi=0{\cdot}474$) and the mean of all ions with from 6 to 44 atoms ($\psi=0{\cdot}388$). For the "ideal" organic cation containing between 4 and 50 atoms, the value of the space-filling number can be taken as 0·40. E. H. R.

Movement of the Ions during Electrolysis. Carlo Del Lungo (*Nuovo Cim.*, 1918, [vi], **16**, ii, 173—181).—By application of Stokes's law to the question of the movement of the ions, the author deduces theoretically Walden's empirical law, according to which, for one and the same electrolyte, the product of the viscosity of the solvent and of the equivalent conductivity, Λ_0, is a constant magnitude independent of the temperature. It is found also that the variation of the conductivity, Λ_0, should depend solely on the variation of the viscosity-coefficient, η, as it may be assumed that, at least within certain limits, change of temperature does not sensibly influence the diameters of the ions. Consequently, the temperature variation of Λ_0 should be virtually the same for all electrolytes in aqueous solution. Not only is the law in general verified for salts, but the temperature-coefficients of conductivity between 18° and 40° have the limiting values $2{\cdot}3.10^{-12}$ and $2{\cdot}6.10^{-12}$, which correspond closely with the temperature-coefficient of the viscosity of water.

Stokes's law allows also of calculation of the diameter of the ions, and the values thus derived are in good agreement with those deduced in accordance with the kinetic theory of gases. In general, the ions are small in comparison with the molecules, but the difference is exceptionally marked with the ions $H^{\cdot}$ and OH', the diameters of which are only about one half of what they should be according to the diameters of the molecules H_2, O_2, and H_2O. The existence of free $H^{\cdot}$ and OH' ions in all aqueous solutions, and perhaps in greater number in solutions of acids and bases, would cause the calculated velocities of the ions of the electrolyte to be greater than the true values; these considerations would explain the exceptionally high values obtained for the transport velocities of the ions $H^{\cdot}$ and OH' and the low values of the corresponding temperature-coefficients, and of the diameters calculated according to Stokes's law. It appears that the ions $H^{\cdot}$ and OH' exist under special conditions different from those shown by other ions, and that the friction between them and water molecules is far less than with other ions.

The dimensions of the ions of the metals and of the non-gaseous non-metals given by Stokes's law are compared with those calculated on the basis of the atomic volumes. The agreement is good for univalent elements, with the exception of potassium, but there

is a moderately high and approximately constant difference in the case of the bivalent metals. T. H. P.

The Decomposition of Dielectric Liquids in the Midst of which an Arc passes. Ed. Urbain and Claip. Scal (*Compt. rend.*, 1919, **168**, 887—889).—An arc, started by a high-frequency spark, and continued by a current at low voltage, in passing through the tetrachloride of titanium, tin, or carbon, causes a marked decomposition, chlorine being liberated. With saturated liquid hydrocarbons, there is a liberation of acetylene, ethylene, and hydrogen, and a deposition of carbon. With pinene, the same products are obtained, and at the same time there is a marked formation of isoprene in the liquid. Ketones yield carbon monoxide and different hydrocarbons. In the case of organic dielectric liquids, the process of decomposition differs according as the liquid is maintained at 15° or at its boiling point, the decomposition being far more thorough in the latter case. W. G.

Thermochemical Application of the Grating Theory. M. Born (*Ber. Deut. physikal. Ges.*, 1919, **21**, 13—24).—A theoretical paper in which it is shown that the formation or decomposition of a crystalline substance must be accompanied by a heat change which is equal to the electrical energy of the grating. It is impossible to calculate this quantity with the hope of finding agreement between the experimental quantity and the calculated quantity of heat, but it is shown in the case of the alkali halogen salts, and also for the calcium halogen salts, that the order of the two quantities is the same. The formation of a crystal of sodium chloride from its elements is considered as occurring in three steps: (1) the subdivision of sodium into isolated atoms and the ionisation of these, which uses a quantity of work Z_{Na}; (2) the subdivision of the chlorine into atoms and the ionisation of these, which absorbs work Z_{Cl}; (3) the combination of the ions of sodium and chlorine to form the solid crystal, whereby the electrostatic crystal energy, U_{NaCl}, is obtained as heat. The heat of formation is then given by $Q_{NaCl} = -Z_{Na} - Z_{Cl} + U_{NaCl}$. It is shown that $\Delta Z_{Na,K} = Z_{Na} - Z_K = U_{NaCl} - U_{KCl} - Q_{NaCl} + Q_{KCl}$ and from this $\Delta Z_{Na,K}$ is independent of the halogen. The value of U is calculated for the lithium haloids, and found to fall from the fluoride to the iodide.

J. F. S.

Thermal Conductivity of Organic Compounds. W. Herz (*Zeitsch. physikal. Chem.*, 1919, **93**, 376—379).—A theoretical paper in which the relationship between the density (d), specific heat (c), and the thermal conductivity (k), as expressed in the equation $k = \eta . c . d$, is considered. It is shown that the quantity k/cd decreases in homologous series of organic compounds with increasing molecular weight and also with increasing molecular diameter. This is in keeping with the assertion of Weber (*Sitzungsber. K. Akad. Wiss. Berlin*, 1885, 809) that this quantity is

inversely proportional to the mean distance between the molecules. The heat capacity ($c.d$) for equal volumes of liquids and the thermal conductivity k are proportional to one another, although many exceptions to this occur. In some liquids, the heat capacity varies inversely as the thermal conductivity. J. F. S.

Equation of State for Liquids and Vapours. I. Vapour Phase of Ethyl Ether. FREDERICK G. KEYES and WILLIAM A. FELSING (*J. Amer. Chem. Soc.*, 1919, **41**, 589—619).—The authors discuss the basal ideas of the kinetic theory in their relationship to the work of van der Waals, and they deduce an equation of state on the present-day conception of the atom. This equation has the form $p=RTx/(v-\delta)-Ax/(v-l)^2$, in which $\delta=\beta e^{-\alpha/v}$ (see *Proc. Nat. Acad. Sci.*, 1917, **3**, 323). It is shown that the strict proportionality between the pressure increment and the temperature increment at constant volume is the only trustworthy test of a system with one molecular type, and that divergence from the linear curve is due to polymerisation or change in the molecular system. The data of Ramsay and Young and other investigators for ethyl ether have been re-calculated on the above formula, and it is shown that the particular form of the mathematical function $\delta=\beta e^{-\alpha/v}$ and the cohesive pressure expression $\phi=A/(v-l)^2$ are both exact. The pt curves for ether have been measured at constant volume, and are shown to be linear within the limits of accuracy of the measurements. From the constants of these curves, the δ-equation and the ϕ-equation have been computed, and the mathematical form deduced for each shown to be exact. Amagat's data have been used to determine the equation for δ (liquid phase) on the assumption that this phase is bimolecular. The ratios of the β- and α-constants have been compared and found to be simple. For one molecule of liquid, the limiting volume correction β_2 is numerically equal to the limiting volume correction of the gas β_1, whilst α_2 is only one half as great as α_1.
J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes. I. J. NARBUTT (*Zeitsch. Elektrochem.*, 1918, **24**, 339—342).—The specific heat and latent heat of fusion of a number of dihalogenated benzenes have been determined. The following numerical results have been obtained: c' is the mean specific heat of the molten substance, c the mean specific heat of the solid, and g the latent heat of fusion. (1) *p*-Dichlorobenzene, $c^{t_1}_{t_2}=0{\cdot}22024+0{\cdot}0003462(t_1+t_2)$, c' between 99·1° and 52·9° is 0·298±0·004, $g=29{\cdot}50\pm0{\cdot}11$ cal.; *o*-dichlorobenzene, $c=0{\cdot}185\pm1\%$ between −21·3° and −75·6°, $c'^{t_1}_{t_2}=0{\cdot}27022\pm0{\cdot}0001512(t_1+t_2)$, $g=21{\cdot}01\pm0{\cdot}14$ cal.; *m*-dichlorobenzene, $c=0{\cdot}186\pm1\%$ between −27·8° and −76·2°, $c'^{t_1}_{t_2}=0{\cdot}27022+0{\cdot}0001512(t_1+t_2)$, $g=20{\cdot}47\pm0{\cdot}14$ cal.; *p*-chlorobromobenzene, $c'=0{\cdot}239\pm0{\cdot}004$ between 99·8° and 64·6°,

$c_{t_2}^{t_1} = 0{\cdot}17066 + 0{\cdot}0002499(t_1 + t_2)$, $g = 23{\cdot}42 \pm 0{\cdot}09$ cal.; *o*-chlorobromobenzene, $c'^{t_1}_{t_2} = 0{\cdot}21497 + 0{\cdot}0001174(t_1 + t_2)$, $c = 0{\cdot}192 \pm 1\%$ between $-15{\cdot}1°$ and $-74{\cdot}8°$, $g = 15{\cdot}44 \pm 0{\cdot}11$ cal.; *m*-chlorobromobenzene, $c' = 0{\cdot}199 \pm 2\%$ at $-75{\cdot}8°$, $c_{t_2}^{t_1} = 0{\cdot}21224 + 0{\cdot}0001174(t_1 + t_2)$, $g = 15{\cdot}34 \pm 0{\cdot}10$ cal.; *p*-dibromobenzene,

$$c_{t_2}^{t_1} = 0{\cdot}13934 + 0{\cdot}0001907(t_1 + t_2),$$

$g = 20{\cdot}84 \pm 0{\cdot}08$ cal.; *o*-dibromobenzene,

$$c'^{t_1}_{t_2} = 0{\cdot}17994 + 0{\cdot}0001070(t_1 + t_2),$$

$c = 0{\cdot}248 \pm 0{\cdot}75\%$ between $0°$ and $-73{\cdot}2°$, $g = 12{\cdot}79 + 0{\cdot}10$ cal.; *m*-dibromobenzene, $c'^{t_1}_{t_2} = 0{\cdot}17535 + 0{\cdot}0001070(t_1 + t_2)$, $c = 0{\cdot}134 \pm 1\%$, $g = 13{\cdot}39 \pm 0{\cdot}09$ cal.; *p*-bromoiodobenzene,

$$c_{t_2}^{t_1} = 0{\cdot}11627 + 0{\cdot}0001576(t_1 + t_2),$$

$g = 16{\cdot}57 \pm 0{\cdot}07$ cal.; *o*-bromoiodobenzene,

$$c'^{t_1}_{t_2} = 0{\cdot}15285 + 0{\cdot}0000666(t_1 + t_2),$$

$c' = 0{\cdot}148 \pm 2\%$ between $0°$ and $-75{\cdot}5°$, $g = 12{\cdot}2 \pm 2\%$; *m*-bromoiodobenzene, $c'^{t_1}_{t_2} = 0{\cdot}15134 + 0{\cdot}0000666(t_1 + t_2)$, $c = 0{\cdot}143 \pm 1\%$ between $-12{\cdot}5°$ and $-74{\cdot}8°$, $g = 10{\cdot}30 \pm 0{\cdot}10$ cal.; *p*-di-iodobenzene, $c_{t_2}^{t_1} = 0{\cdot}10093 + 0{\cdot}0001332(t_1 + t_2)$, $g = 16{\cdot}21 \pm 0{\cdot}10$ cal.; *o*-di-iodobenzene, $c'^{t_1}_{t_2} = 0{\cdot}13574 + 0{\cdot}0000388(t_1 + t_2)$, $g = 10{\cdot}20 \pm 0{\cdot}05$ cal.; *m*-di-iodobenzene, $c_{t_2}^{t_1} = 0{\cdot}10093 + 0{\cdot}0001332(t_1 + t_2)$, $c' = 0{\cdot}140 \pm 0{\cdot}002$ between $99{\cdot}6°$ and $34{\cdot}2°$, and $0{\cdot}137 \pm 0{\cdot}003$ between $63{\cdot}2°$ and $34{\cdot}2°$, $g = 11{\cdot}55 \pm 0{\cdot}03$ cal. The trustworthiness of the formulæ is tested by calculation of the mean specific heat for each set of experimental conditions, and the results in each case are well in accordance with the experimental values. J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes. II. J. Narbutt (*Zeitsch. Elektrochem.*, 1918, **24**, 342—354. Compare preceding abstract).—A theoretical paper in which the results recorded in the previous paper are discussed. The specific heats of the liquid isomerides of the dihalogenated benzenes are practically the same, whereas theoretically they could differ somewhat. The specific heat of very strongly supercooled dihalogenated benzenes changes according to the same rule as is followed above the freezing point. A formula is deduced for calculating the specific heat of nearly related non-associated compounds. This formula has been tested in the case of the dihalogenated benzenes. The dihalogenated benzenes, according to the rule of Longinescu (A., 1908, ii, 931), are non-associated. The critical temperature and the critical volume of several of the dihalogenated benzenes have been calculated; the following values are recorded, which are the mean of the values of the three isomerides: dichlorobenzene, T_k 689°, ϕ 2·43; chlorobromobenzene, T_k 725°, ϕ 1·95; dibromobenzene, T_k 760°, ϕ 1·65; bromoiodobenzene, T_k 809°, ϕ 1·45; chloroiodobenzene, T_k 774°, ϕ 1·66; and di-iodobenzene, T_k 858°.

J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes. III. J. NARBUTT (*Zeitsch. Elektrochem.*, 1919, **25**, 51—57. Compare preceding abstracts).—A theoretical consideration of the results recorded in part I. It is shown that the latent heat of fusion of the dihalogen benzenes decreases in general with increasing molecular weight and decreases with increasing melting point. The mean value of the quotient of the molecular latent heat, M, and the absolute melting point, T, $M/T=\phi$, has the value 13·3 for the para-series, 11·8 for the ortho-series, and 12·0 for the meta-series. The mean values do not differ very much from the individual values, consequently the latent heat of fusion can be calculated for those cases where it has not been experimentally determined. The eutectic points of the system *p*-dichlorobenzene–*p*-di-iodobenzene have been calculated and found to correspond closely with the experimental values. In some cases, the maximum work of solidification has been calculated from the data obtained for the supercooled liquids. The difference between the molecular volumes in the liquid and solid state has been calculated for several of the dihalogenated benzenes. In the case of the para-dihalogenated benzenes, the quotient of molecular latent heat of fusion and the absolute melting point is three times as large as the difference between the molecular heats at the melting point, whilst it is equal to the difference of the mean molecular heats between the melting point and the absolute zero. J. F. S.

Specific Heat and Latent Heat of Fusion of the Dichloro-, Chlorobromo-, Dibromo-, Bromoiodo-, and Di-iodo-benzenes. IV. J. NARBUTT (*Zeitsch. Elektrochem.*, 1919, **25**, 57—66. Compare preceding abstracts).—A mathematical consideration of the experimental results recorded in part I. It is shown that in general the solid isomerides of the dihalogenated benzenes have practically the same specific heat over the temperature range examined, but in some cases a markedly different value is obtained. The dependence of the specific heat on the temperature is greater in the solid state than in the liquid state. The specific heat changes quite regularly with temperature even in the neighbourhood of the melting point. The mean specific heat cannot be calculated by the Neumann rule to nearer than 2% even when the dependence of this factor on temperature is taken into account. The value of β_v of the Nernst and Lindemann formula has been calculated for the various atoms, and the following values obtained: C (attached to H) 3100, C (attached to a halogen) 1400, H (attached to C) 850, Cl (attached to C) 365, Br (attached to C) 250, and I (attached to C) 100. These values are, however, not trustworthy for calculations involving extrapolation to very low temperatures. The work of expansion against the cohesive forces is the same for the gram-molecule of the solid dihalogenated benzenes. J. F. S.

Latent Heats of Fusion and their Relation to Molecular Composition. Harbord George Wayling (*Phil. Mag.*, 1919, [vi], **37**, 495—497).—The latent heat of fusion multiplied by the molecular number (that is, the sum of the atomic numbers of the atoms in the molecule) and divided by the absolute melting point is for many compounds equal to the number of the atoms in the molecule. Thus for water $80 \times 10 \div 273 = 2{\cdot}93$. For the majority of salts with water of crystallisation, the rule holds if two instead of three is allowed for the number of atoms in the water molecule. The generalisation holds for a number of inorganic salts and for formic acid and chloroform. Acetic acid, phenylacetic acid, and butyric acid all yield the same number, 5, but no simple connexion occurs for the closed-ring or aromatic compounds. F. S.

Cryoscopic Investigation of Double Salts and Complex Salts in Aqueous Solution. E. Cornec and G. Urbain (*Bull. Soc. chim.*, 1919, [iv], **25**, 131—136).—A more detailed account of work already published (compare A., 1914, ii, 428). W. G.

The Measurement of Very Low Temperatures. XXIX. Vapour Pressures of Oxygen and Nitrogen for obtaining Fixed Points on the Temperature Scale below 0°. P. G. Cath (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 656—663).—The vapour pressures of oxygen and nitrogen have been determined at temperatures in the neighbourhood of 57° to 90° (abs.). In the case of oxygen, the results can be expressed by the equation $\log p = A/T + B + CT$ (p in atm.), with $A = -419{\cdot}31$, $B = 5{\cdot}2365$, $C = -0{\cdot}0648$. From this equation, the normal boiling point of oxygen would be 90·13° on Kamerlingh Onnes' scale, the actually observed value being 90·14°. The nitrogen results can be expressed by a similar equation, in which $A = -334{\cdot}64$, $B = 4{\cdot}6969$, and $C = -0{\cdot}00476$. The boiling point of nitrogen calculated from the equation is 77·31° on the same scale. Measurements of the vapour pressure of solid nitrogen give the relation $\log p = -358{\cdot}73/T + 4{\cdot}7769$ as holding near the triple point. This equation gives for the triple point $T = 63{\cdot}25°$, $p = 0{\cdot}1269$ atm., or 9·64 cm. E. H. R.

Vapour Pressure and Latent Heat of Vaporisation of Silicon Hydrides and their Simple Derivatives. Robert Wintgen (*Ber.*, 1919, **52**, [*B*], 724—731. Compare Stock, Somieński, and Wintgen, A., 1918, ii, 110, 111).—A mathematical investigation of the data recorded by Stock and his co-workers on the vapour tension at various temperatures of simple silicon compounds, and the calculation of the molecular latent heat of vaporisation of the substances at any temperature. H. W.

Vapour Pressure Regularities. II. W. Herz (*Zeitsch. Elektrochem.*, 1918, **24**, 333—335).—The proportionality factor of Dühring's rule has been calculated for the substances chlorine, bromine, iodine, argon, krypton, xenon, oxygen, sulphur, nitrogen,

phosphorus, arsenic, bismuth, copper, silver, zinc, cadmium, mercury, tin, lead, and a large number of organic substances. It is shown that in all cases it exhibits an approximate constant. In the case of the non-metals, the q value increases with increasing pressure, and in every group of the periodic system with increasing atomic weight. The metals behave in the opposite way. The q value for compounds in most cases exhibits a tendency to increase with increasing molecular weight in each group of the periodic system and in each homologous series of organic substances. J. F. S.

Molecular Theory of the Vapour Pressure of Solid Substances and its Significance in the Calculation of Chemical Constants. Otto Stern (*Zeitsch. Elektrochem.*, 1919, **25**, 66—80).—A mathematical paper in which a theory of the vapour pressure of solid substances is developed on the basis of the following four hypotheses: (i) The attractive forces between atoms in the gaseous phase may be neglected on account of the relatively great distance between the atoms. (ii) The atoms exercise attractive forces on one another in the solid phase, and these forces are in equilibrium about the centres of gravity of the atoms. In the case of crystals, these forces are arranged orderly in the crystal grating. (iii) The atomic forces operate so that when an atom moves from its position of equilibrium, an opposing force is set up which tends to bring it back into the position of equilibrium. The magnitude of this force is proportional to the amount of movement of the displaced atom. (iv) To move an atom from its position of equilibrium, a definite finite amount of work, ϕ_0, is necessary, so that $N\phi_0=\lambda_0$ is the heat of sublimation at the absolute zero, on the assumption that at this point all atoms are in their equilibrium positions. Complicated formulæ are developed on these assumptions, and these take account of the different frequencies of the atoms. From these formulæ others are developed for calculating the chemical constants. J. F. S.

Vapour Pressure of Acetone-Chloroform Mixtures. Alfred Schulze (*Zeitsch. physikal. Chem.*, 1919, **93**, 368—375).—The vapour pressure of various mixtures of acetone and chloroform has been determined at 30°, 70°, and 90°, and composition–pressure curves constructed for the three temperatures. The curves indicate that acetone–chloroform mixtures contain an equimolecular compound of the two constituents in a dissociated condition, which with increasing temperature apparently becomes less. At 30°, a distinct association of acetone is noticeable. By the aid of the law of mass action, the vapour pressure of the various mixtures was calculated, and the results shown to be in good agreement with the experimental values. J. F. S.

Explosion, Implosion, and Bursting. Walter Brieger and Hans Schimank (*Zeitsch. Elektrochem.*, 1918, **24**, 354—356. Compare A., 1917, ii, 462).—A discussion on the exact definition of

the term explosion. An explosion is defined as the sudden development of a gaseous volume, an implosion as the sudden disappearance of a gaseous volume. Bursting may be occasioned by either process or by inequalities of pressure or strain. J. F. S.

Calculation of the Density of some Elements at the Absolute Zero. W. Herz (*Zeitsch. anorg. Chem.*, 1919, **105**, 171—174).—The densities and atomic volumes of a number of elements at absolute zero have been calculated, making use of Lorenz's relation between the volume at absolute zero and that at the critical point, boiling point, and melting point (A., 1916, ii, 312). These relationships are given by the equations $d_0=1{\cdot}41d_s=3{\cdot}75d_k=1{\cdot}21d_e=d(0{\cdot}77+0{\cdot}64T/T_s)$, in which d is the density, T is the absolute temperature, and the suffixes o, s, k, and e represent, respectively, absolute zero, boiling, critical, and melting points. The values of d_0 calculated from the different equations do not always show very good agreement; in the case of mercury, for instance, d_0 varies between 14·23 and 17·41. It is claimed, however, that in most cases a very fair approximation to the true value is obtained. Sodium (1·083) has a greater zero density than potassium (1·004), but in all other cases the density increases with the atomic weight. E. H. R.

Physical and Chemical Theories [of the Action of Toxins, Dyes, etc.]. I. Traube (*Chem. Zeit.*, 1919, **43**, 129—130).—Polemical. A continuation of the controversy with Karrer (Traube, A., 1912, ii, 740; Karrer, A., 1918, ii, 431).

Measurement of the Thickness of Film formed on Glass and Sand. Earl Pettijohn (*J. Amer. Chem. Soc.*, 1919, **41**, 477—486).—A method is described by which the thickness of a film of liquid, capable of forming on the surface of sand and glass beads without free liquid being present, may be measured. The method consists in placing a known weight of sand (200 grams) in a dry, conical flask and adding the liquid drop by drop from a burette with repeated shaking after each addition until particles of the sand adhere to the walls of the flask. The adherence to the walls is taken to indicate the presence of free liquid. The surface of the sand or beads is then determined, and the thickness of the film calculated. These experiments were carried out with water, nitrobenzene, aniline, dimethylaniline, iodobenzene, toluene, turpentine, and pyridine, and with sands and beads of varying diameter. The results show that there is no chemical combination between the liquid and the solid. The thickness of the film is independent of the liquid used and of the size of the solid particles. J. F. S.

Formulæ concerning Surface Tension. Arthur C. Lunn (*J. Amer. Chem. Soc.*, 1919, **41**, 620—621).—A theoretical discussion on the mathematical processes involved in the deduction of the formulæ used for calculating surface tension. J. F. S.

Determination of Surface Tension (Free Surface Energy), and the Weight of Falling Drops: Surface Tension of Water and Benzene by the Capillary Height Method. WILLIAM D. HARKINS and F. E. BROWN (*J. Amer. Chem. Soc.*, 1919, **41**, 499—524).—The two methods in general use for the determination of surface tension are considered, the errors attached to each method are indicated, and a series of determinations of the surface tension of water and benzene are recorded. The theory of the capillary rise method is simple, but the technique is difficult, and its use in some cases causes errors as high as 30%, due to its inapplicability to certain classes of substances. The drop-weight method is applicable to a wide range of liquids, and the technique is not difficult; but the theory of this method has not been completely worked out, so that many of its published results are inaccurate, although the experimental data are accurate; this is due to the use of an inaccurate theory. The relation of the experimental results of the drop-weight method to those of the capillary rise method has been determined by using liquids which give accurate results by both methods, and this relationship has been plotted in such a way as to show the relation between surface tension and the form of the drop which falls from a circular tip. The surface tension and the capillary constant of water and benzene at 20°, each against air saturated with its own vapour, have been determined by the capillary rise method. The values obtained are: for water, $\gamma=72{\cdot}800$ dynes per cm., $a^2=14{\cdot}897$ mm.; for benzene, $\gamma=28{\cdot}80$ dynes per cm., $a^2=6{\cdot}713$ mm. In this determination, the capillary tubes were steamed out with the vapour of the liquid before use. In the case of water, this increased the value of γ by about 0·1 dyne. Water, benzene, carbon tetrachloride, and ethylene dibromide were dropped from a large number of glass and metal tips of radii varying from 0·09946 cm. to 1·0028 cm., and the weights of the falling drops determined. From the data, r/a and $f(r/a)$, of the Lohnstein equation,

$$Mg=2\pi r\gamma f(r/a),$$

were calculated for values of r/a between 0·25 and 2·60. The value of $f(r/a)$ is not constant, but varies from 0·7256 to 0·5352 in this range, whilst when r/a falls to 0·025, $f(r/a)$ rises to 0·924. It is assumed that in conjunction with other necessary conditions, r/a really determines the shape of the hanging drop, and that it is the shape of the drop which determines the fraction of the drop which falls. This shape may also be determined by the ratio of r to the cube root of the volume of the falling drop. Thus a new equation, similar to that of Lohnstein, was derived,

$$Mg=2\pi r\gamma\psi(r/v^{\frac{1}{3}}).$$

This is more easily applied to the determination of surface tension than Lohnstein's equation, since all the factors except γ are obtained by direct experiment or from a table of values, whilst the a of Lohnstein's equation cannot be obtained from the direct results of the drop-weight measurements, but must be calculated by methods of approximation. J. F. S.

Osmotic-kinetic Theory of Dilute Solutions. G. JÄGER (*Zeitsch. physikal. Chem.*, 1919, **93**, 275—311).—A theoretical paper in which the relationship between pressure and volume of a highly compressed gas is deduced. It is shown both as a first approximation and also strictly that that portion of the pressure of a highly compressed gas occasioned by the arrangement of the molecules on a surface can be calculated as though no collisions between the molecules occurred. To this portion of the pressure there is to be added that occasioned by the collisions of the molecules. The sum of the two gives the pressure exerted on the walls of the containing vessel. Calculations show that for a solution an osmotic pressure is obtained which is the same as the value which would be obtained if the dissolved substance alone were present in the vessel. It is also shown that a dilute solution must have the same internal pressure as the pure solvent. The equations for the elevation of the boiling point and the lowering of the freezing point are developed from the vapour-pressure lowering. It is also shown that the Nernst theorem can be obtained from kinetic considerations, and that the relationship of the concentrations of a non-electrolyte in two sparingly soluble solvents is independent of the quantity of dissolved substance. J. F. S.

Rapid Determination of Solubility. T. J. WARD (*Analyst*, 1919, **44**, 137).—About 3 c.c. of the solvent are heated in a test-tube placed in a beaker of water about 10° to 20° higher than the temperature at which the solubility is to be determined, and small quantities of the substance are added, with constant shaking, until some remains undissolved. The test-tube is then immersed in water at the desired temperature for ten minutes, with occasional shaking, after which a thimble of filter-paper is pushed into the tube so that the liquid can filter inwardly. A definite volume of the filtrate is withdrawn by means of a pipette, weighed in a covered vessel, and evaporated, and the residue dried and weighed. C. A. M.

Coagulation of Metal Sulphide Hydrosols. I. Influence of Distance between the Particles of a Sol on its Stability. Anomalous Protective Action of Dissolved Hydrogen Sulphide. JÑANENDRA NATH MUKHERJEE and NAGENDRA NATH SEN (T., 1919, **115**, 461—472).

The Chemical Equilibrium between Lead Sulphide and the Products of the Roasting Process. RUDOLF SCHENCK and AGNES ALBERS (*Zeitsch. anorg. Chem.*, 1919, **105**, 145—166).—The three-component system lead–sulphur–oxygen gives rise to seven solid phases, Pb, PbO, PbS, $PbSO_4$, $PbSO_4$,PbO, $PbSO_4$,2PbO, $PbSO_4$,3PbO, besides the gaseous phase SO_2. There are thirteen possible univariant systems, each consisting of three solid phases in equilibrium with the gaseous phase, and these

thirteen systems fall into three groups. In group I (4 systems), lead sulphide is in equilibrium with two oxygen-containing phases; in group II (5 systems), lead sulphide and metallic lead are in equilibrium with one oxygen-containing phase; and in group III (4 systems), metallic lead with two oxygen-containing phases. The vapour-tension curves for the systems of groups I and II have been investigated at temperatures between 500° and 820°. Earlier measurements of the vapour tensions of some of these systems were made by Schenck (A., 1907, ii, 546, 619) and Reinders (A., 1915, ii, 47), but their results were to some extent vitiated through the use of silica vessels, which were attacked by the reaction mixtures. This difficulty has been overcome by the use of calcium phosphate for the containers. The pressure–temperature diagram for the nine systems investigated is given. The most stable phases are those of group II, in which both lead and lead sulphide are present as solid phases, these systems being in equilibrium with a lower pressure of sulphur dioxide than those of group I. The vapour phase always contains lead sulphide. It follows that in the systems of group III, in which lead sulphide is not present as a solid phase, the vapour must be unsaturated with respect to lead sulphide. A complete equilibrium diagram, including the systems of group III, must therefore be in three dimensions, the third co-ordinate representing the vapour pressure of lead sulphide. It was found impossible to realise experimentally the conditions of existence of the systems of group III, as they are apparently very unstable.

The vapour pressure of lead sulphide between 850° and 1000° was measured, and was found to increase from 2 mm. to 17 mm. between these temperatures. Lead sulphide distils readily in a vacuum at 900°. E. H. R.

The Action of Salts. K. Spiro (*Biochem. Zeitsch.*, 1919, **93**, 384—394).—Many ions may have an influence on quite simple chemical reactions in which they are apparently not directly concerned. The influence of the ions may be arranged in order of magnitude, resembling the Hofmeister series.

The reactions studied included the oxidation of potassium iodide by atmospheric oxygen and hydrogen peroxide, the oxidation of indigo, the guaiacum reaction, the reducing action of hydrogen peroxide on ferric chloride and potassium ferricyanide, the oxidation of ammoniacal cuprous and silver oxides by dextrose, the indophenol reaction, and the action of catalase. The series of ions are not identical in every case. The presence of magnesium may in certain cases exert a more favourable action on oxidation processes than that of sodium, but examples of the reverse condition occur. Certain examples of the influence of foreign ions may be considered to be analogous to co-enzyme actions. It is apparent, however, that the lyotropic series may apply for simple chemical reactions as much as for physico-chemical reactions, such as imbibition or emulsification. J. C. D.

Catalytic Action of Hydrogen Ions in Hydrolyses. Rud. Wegscheider (*Ber.*, 1919, **52**, 235—236).—The failure of hydrogen ions to catalyse the hydrolysis of β-lactones is not the first example of abnormality in hydrion catalysis (see Johannson and Sebelius, A., 1918, ii, 223). Sulphonic esters are also known to be uninfluenced in this way, although the hydrolysis of alkyl hydrogen sulphates is catalysed by hydrions. J. C. W.

Temperature-coefficient of Catalysed and Non-catalysed Reactions. N. R. Dhar (*Ann. Chim.*, 1919, [ix], **11**, 130—223).—A more detailed account of work already published (T., 1917, **111**, 707). W. G.

Conception of Chemical Elements and Atomic Weight Tables. Rud. Wegscheider (*Zeitsch. physikal. Chem.*, 1919, **93**, 380—381).—Polemical against the definition of the term element put forward by Paneth (compare A., 1916, ii, 240; 1918, ii, 304). J. F. S.

Valency Theory. A. E. Lacomblé (*Zeitsch. physikal. Chem.*, 1919, **93**, 257—274).—A theoretical paper in which, on the basis of Kossel's (A., 1916, ii, 243) conception of the atom, the author develops a theory of valency. As hypothesis, the following assumptions are made: (i) The electrons situated on the outside ring are stationary. (ii) A sphere is supposed to surround the atom in such a way that its centre lies at the centre of gravity of the atom, and only the outermost sheath falls outside the atom. The field of forces of the nucleus is regarded as that of a sphere of stated size having on its surface an irreplaceable positive charge of dimensions equal to, but opposite in sign to, the sum of the electrons on the outermost sheath. (iii) Chemical combination is regarded as the replacement of the curved lines of force between atoms and their electrons by shorter and straight lines of force. On the basis of these assumptions, the nature of the compounds which are formed between various elements is deduced. For example, it follows that the stability of the oxygen derivatives of the halogens increases with increasing atomic weight of the halogen. The halogen derivatives of the elements of group 6 increase in stability with increasing atomic weight of the element of the sixth group. Many other cases are developed. The nature of the bonds in the formation of molecules of elements is considered. This is divided into three types, which differ in the density of the lines of force on the atoms. The paper concludes with a description of the nature of the bonds of organic compounds. J. F. S.

The Mythical Basil Valentine. W. Hommel (*Zeitsch. angew. Chem.*, 1919, **32**, i, 73—76).—Although the existence of the alleged fifteenth-century monk, Basil Valentine, was doubted by Gmelin (1797), and by Kopp in his later work (1886), he is still, in many quarters, regarded as the last of the alchemists.

Anachronisms in the supposed writings of Basil Valentine prove that these could not have been written as early as 1460. All the evidence indicates that the name was a pseudonym for Johann Thölde, who, in 1603—1604, first published the writings of "Basil Valentine." The survival of the myth down to the present day is largely attributable to the account in Kopp's "Geschichte der Chemie" (1843), whilst Kopp's later conclusion on the subject has been overlooked. C. A. M.

Simple Efficient Vacuum Pump for Laboratories. Max Volmer (*Ber.*, 1919, **52**, [*B*], 804—809).—The pump is constructed on principles similar to those of Langmuir (*Phys. Rev.*, 1916, **8**, 48) and Kraus (A., 1917, ii, 567), from which it differs considerably in detail. The mercury is boiled in a glass vessel, and the vapour, passing through a narrow tube into the cooling chamber, carries with it the air from the vessel to be exhausted and passes it into the fore-vacuum of a water pump; the condensed mercury flows back by a side-tube to the bottom of the boiler, direct connexion between the fore- and main-vacua being prevented by a bent tube, in which mercury collects. The apparatus is figured in the original.

The average efficiency of the pump is such that a litre flask can be exhausted from 15 mm. to $<1/100$ mm. in five minutes, but differs somewhat with different individuals, as it depends on small factors which cannot invariably be reproduced. It is easily manipulated and cleaned. Vapours are removed as readily as gases, and it is not sensitive to moderate amounts of halogens. Its use is recommended for drying substances and for distillation under greatly diminished pressure. By the aid of the pump, more complete desiccation can be effected in thirty minutes than by exposure to alkali hydroxide at 10 mm. during twenty-four hours. H. W.

Gas Washing Flask, especially for Use in the Estimation of Sulphur Dioxide in Flue Gases. H. Schilling (*Chem. Zeit.*, 1919, **43**, 167).—The central inlet tube and the exit tube leading from the stopper of the flask are connected by means of a short length of tube provided with a tap. By means of the latter, when suitably turned, the gases may be directed through the solution contained in the flask or passed directly through the connecting tube and tap without entering the flask. W. P. S.

Very Simple Form of Electrolytic Current Interrupter for Demonstration Purposes. Karl Brunner (*Ber.*, 1919, **52**, [*B*], 629—630).—The apparatus consists of a glass trough with parallel sides, holding about 2 litres; on the one side, a lead plate, 9×13 cm., is suspended in 8% sulphuric acid. A board, laid on the top of the vessel, serves as adjustable support for a glass tube of 16 mm. diameter, at the bottom of which a hole, 3—4 mm. in diameter, is blown. The hole is partly closed by a pointed glass

rod, 50 mm. long and weighing 0·9 gram, which forms a valve opening in the upward direction. A strip of lead, 10 mm. wide, extends to the bottom of the tube. The apparatus is readily constructed from available material. In comparison with the Wehnelt interrupter, it gives a rather shorter spark, but is more trustworthy and less noisy in action. H. W.

Lecture Experiment [Combustion of Phosphorus]. KARL BRUNNER (*Ber.*, 1919, **52**, [*B*], 631—632).—The phenomena attending the combustion of phosphorus are conveniently and safely demonstrated in the following manner. The apparatus consists of two doubly tubulated glass vessels holding about a litre, which are connected by a short length of slightly bent quartz tube; the other tubulures carry a mercury manometer and a stopcock respectively. About 0·5 gram of yellow phosphorus is placed in the quartz tube, and the complete apparatus is accurately counterpoised. The phosphorus is ignited by gently warming the tube, and slow combustion is maintained by occasional gentle warming of the glass vessels. When combustion is complete, the apparatus is left to itself until the manometer indicates a deficiency in internal pressure. The weight is found to be unaltered. The stopcock is now opened, when a distinct increase in weight is caused by the inrushing air. H. W.

Preparation of Phosphorus Trioxide as a Lecture Experiment. HEINRICH BILTZ and ANNA GROSS (*Ber.*, 1919, **52**, [*B*], 762—768).—The apparatus consists of a combustion tube, 30 cm. long and 1·8—2·0 cm. internal diameter, which is drawn out to a point and turned upwards at one end. This is connected with a filter tube, 25 cm. in length and of the same diameter as the first tube, which contains a loose plug of cotton wool and a layer of 6 cm. of tightly compressed cotton-wool balls. During the experiment, the tube (which is preferably made of brass) is heated at 50—60° by a small flame. A condensation tube, 75 cm. long and 2 cm. wide, is connected with the filter tube and, through a wash-bottle containing sulphuric acid, to a filter pump. About 10 grams of phosphorus are placed in the combustion tube, the filter tube is warmed, and the experiment started by gently warming the phosphorus until it is just ignited; after about two minutes, when the tube has become warmed, the speed of the air stream is considerably increased. After five to ten minutes, phosphorus trioxide begins to appear in the condensation tube, which is cooled, if necessary, by a cloth dipped in ice-water. The experiment must be stopped before the phosphorus is completely burnt; if not, oxygen gets access to the phosphorus trioxide and causes oxidation. The crystalline nature and low m. p. of the trioxide are readily demonstrated; the oxidisability is shown by opening the tube in the dark, when a luminescence is shown which develops into active combustion when the tube is warmed or by dissolving the substance

in carbon disulphide, so as to obtain a dilute solution, which is then poured on to filter paper.

The authors are led to the conclusion that phosphorus trioxide is always the primary product of the combustion of phosphorus, and that formation of the pentoxide is a subsequent reaction. They therefore recommend the use of a rapid air current, since this ensures on the one hand a rapid combustion, and consequent complete removal of oxygen from the residual gases, and on the other a rapid withdrawal and cooling of the phosphorus trioxide, which is otherwise readily decomposed into phosphorus pentoxide and red products.

The yield of phosphorus trioxide is only moderate, and the addition of indifferent gases, either before or behind the zone of combustion, does not effect sufficient improvement to justify the complication involved. H. W.

Inorganic Chemistry.

Hypochlorous Acid and Chlorine Monoxide. Stefan Goldschmidt (*Ber.*, 1919, **52**, [*B*], 753—761).—Aqueous solutions of hypochlorous acid containing 25% of the acid are readily obtained by distilling a mixture of chlorine hydrate and yellow mercuric oxide in a good vacuum; attempts to prepare the more concentrated solution or the anhydrous acid by distillation of this acid in a moderate vacuum, and condensation of the distillate in receivers maintained at 0°, −20°, and −80°, led to an unexpected result, since in the first two vessels aqueous hypochlorous acid (25%) was collected, whilst in the third vessel pure chlorine monoxide was condensed (the pure monoxide has b. p. +3·8°/766 mm. and can only be preserved without decomposition for any length of time at −80°). It therefore appeared that the aqueous acid contains two systems in equilibrium: (1) $HClO \rightleftharpoons \overset{+}{H} + \overset{-}{O}Cl$, and (2) $HClO \rightleftharpoons Cl_2O + H_2O$. The latter system has been investigated by agitating aqueous hypochlorous acid solutions of different concentration with an equal volume of carbon tetrachloride at 0°, separating the solutions, and estimating the active chlorine in each by titration with sodium thiosulphate after treatment with acidified potassium iodide solution. The equilibrium lies greatly in favour of the hypochlorous acid, so that an approximately *N*/5-solution contains 0·02% of the anhydride.

The well-known greater oxidising power of hypochlorites in acid than in alkaline solution is probably due to chlorine monoxide contained in the former solutions. H. W.

Preparation of Sulphuryl Chloride. A. Boake Roberts and Co., Ltd., and Thomas Harold Durrans (Brit. Pat., 124542).—Sulphur dioxide and chlorine, in equal volumes, are passed either together or alternately, and either continuously or intermittently, into a vessel containing a suitable catalyst. The temperature must be kept sufficiently low to prevent the catalyst and the sulphuryl chloride formed from volatilising, and sufficiently high to prevent the catalyst from solidifying. The sulphuryl chloride may be isolated by distillation or other suitable means.

The following classes of substance are effective as catalysts, and do not require the aid of light or pressure, the most suitable members of each class being placed within brackets: terpene hydrocarbons (pinene and limonene); esters which are compounds of saturated acids or of monohydroxyphenols with monobasic aliphatic acids containing carbon, hydrogen, and oxygen only (methyl acetate, *iso*amyl formate, ethyl butyrate, phenyl acetate, phenylethyl acetate, glyceryl triacetate, oils which are esters of glycerol, and also triphenyl phosphate and tritolyl phosphate); ethers which are the mixed or simple saturated aliphatic ethers (ethyl ether, *iso*butyl ether, benzyl ether, tolyl ether), and the terpene ether, cineole (eucalyptol); the saturated monohydroxyphenols which contain only one benzene ring. The ethers, phenols, and esters are limited to those which contain carbon, hydrogen, and oxygen only, and no substituting groups except those containing only carbon and hydrogen. [See also *J. Soc. Chem. Ind.*, 1919, June.]

H. W.

Colloidal Selenium. Julius Meyer (*Zeitsch. Elektrochem.*, 1919, **25**, 80—82).—Colloidal selenium may be obtained by the action of dilute sulphuric acid on sodium selenosulphate according to the equation $Na_2SeSO_3 + H_2SO_4 = Se + SO_2 + H_2O + Na_2SO_4$. A small quantity of sodium sulphite is dissolved in 5 c.c. of distilled water and boiled with an equal quantity of selenium for about half a minute, the solution is filtered, and about 1 c.c. of the filtrate diluted with a litre of water, treated with four to five drops of dilute sulphuric acid, and stirred. The solution becomes at once orange-yellow to dark red in colour, depending on the concentration. Filtration through a Zsigmondy membrane gives a clear, colourless sol. The sols are very stable and not at all sensitive to moderate concentrations of acids. The particles are positively charged, and thus differ from the colloidal selenium produced by the solution of selenium in hydrazine hydrate, which is negatively charged. A comparison of the two forms of colloidal selenium is given in the paper, and the suitability of the new form for lecture experiments is demonstrated. J. F. S.

The Decomposition of Nitrous Acid. Joseph Knox and Douglas M. Reid (*J. Soc. Chem. Ind.*, 1919, **38**, 105—108T).—The nitrous acid solutions for these experiments were prepared by mixing solutions of nitric acid and sodium nitrite of known

strengths. The rate of decomposition of the nitrous acid was found to be profoundly influenced by the conditions. It is greatly accelerated when the amount of surface exposed to the action of air is increased, for example, by shaking in presence of excess of air. The excess of air is effective through removing by oxidation the nitric oxide produced in the reversible reaction, $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$, thus allowing the balanced reaction to proceed in the direction from left to right. The nitric oxide can also be removed from the solution by the passage of a current of carbon dioxide, the decomposition being accelerated almost as much as by a current of air. The influence of temperature on the rate of decomposition with, and without, excess of air was studied up to 50°, and the rate was found to increase rapidly with the temperature. Free nitric acid, if present, accelerates the initial rate of decomposition of the nitrous acid, but appears to have a retarding influence in the later stages. The several series of experiments are illustrated by curves. E. H. R.

Densities of Mixtures of Sulphuric and Nitric Acids. Paul Pascal and M. Garnier (*Bull. Soc. chim.*, 1919, [iv], **25**, 142—145).—Tables are given showing the results of determinations of the density of sulphuric and nitric acids at different concentrations, and of mixtures of these acids in varying proportions and with varying proportions of water added. It is shown that, in the zone of mixtures used for nitrating cotton, the density is almost entirely a function of the water content. W. G.

Baeyer's Strain Theory and the Structure of the Diamond. Ernst Mohr (*J. pr. Chem.*, 1918, [ii], **98**, 315—353).—A theoretical paper in which the stability of the *cyclo*hexane ring is first considered; it is shown that the number of known isomerides is readily explicable by means of Lachse's model (in which the carbon atoms do not lie in one plane) if, at the same time, a free or only partly hindered rotation is assumed. The ideas are extended to more complex rings, but the data are too restricted to allow any very general conclusions to be drawn.

It is further shown that atom model systems can be constructed by the direct or oblique superposition of *cyclo*hexane ring layers in the centre of which all valencies are saturated without strain and in which free valencies exist only at the surface. The diamond space lattice described by Bragg is then found to be identical with the obliquely formed carbon atom system so derived.

The existence of carbon rings which contain more than six carbon atoms and which are free from strain is also considered, but the author is led to the conclusion that the strain in such systems cannot at present be predicted with any certainty, and is probably complicated by other factors. H. W.

Attempted Synthesis of Carbonyl Sulphide by means of the Electric Spark. F. González and E. Moles (*Anal. Fis. Quím.*, 1919, **17**, 55—59).—The assertion of Chevrier (*Compt.*

rend., 1869, **69**, 136) that sulphur vapour and carbon monoxide combine easily under the action of the electric spark to form carbonyl sulphide was tested by the authors. Pure dry carbon monoxide was passed in a sealed apparatus over the surface of sulphur heated at 110° and 260°, and there subjected to sparking. The gaseous products were cooled in various freezing mixtures, finally in liquid air. No trace of carbonyl sulphide was observed. An experiment under reduced pressure also yielded a negative result.

W. S. M.

Thermal Decomposition of Carbonyl Sulphide. Alfred Stock and Paul Seelig (*Ber.*, 1919, **52**, [*B*], 681—694).—The thermal decomposition of carbonyl sulphide leads to the formation of carbon monoxide and sulphur on the one hand and to carbon dioxide and carbon disulphide on the other; assuming that carbon oxysulphide is immediately concerned with each equilibrium, the reactions may be written $2COS \rightleftarrows 2CO + S_2$ and $2COS \rightleftarrows CO_2 + CS_2$. Attempts have now been made to determine the equilibrium at 800° and 950° respectively. For this purpose, a current of carbonyl sulphide is sent through an electrically heated quartz tube packed with quartz splinters and provided with a quartz rod to prevent backward diffusion of gas; the end of the quartz tube is drawn out to a capillary connected as closely to the furnace as possible with a quartz **U**-tube, which is immersed in a paraffin bath maintained at 130°, and serves to retain the sulphur; the gases evolved are collected over mercury and analysed by the authors' method (this vol., ii, 245). The effect of the rate of passage of gas (time of heating) and rapidity of cooling (length of capillary) has been investigated, from which it appears that the values observed approximate closely to the true equilibria values.

At 800°, the reaction $2COS \rightleftarrows CO_2 + CS_2$ appears to proceed slowly in either direction, whilst the action $2COS \rightleftarrows 2CO + S_2$ is very rapid. The fact that the carbon monoxide degree of dissociation is independent of the amounts of carbon dioxide and carbon disulphide present shows that carbon monoxide and sulphur (at any rate for the greater part) are primary products of the decomposition of carbonyl sulphide, and not formed secondarily from carbon dioxide and carbon disulphide. The CO_2 degree of dissociation is about 48·5%, the CO degree about 45·5%, so that, at 800° and atmospheric pressure, the carbonyl sulphide is decomposed to the extent of about 64%. At 950°, the corresponding figures are 43% for the CO_2 degree of dissociation, at least 71% for the CO degree, and at least 76% for the dissociation of carbon oxysulphide.

[With W. Ottmann.]—Preliminary experiments on the action of heat on mixtures of carbon dioxide and disulphide on the one hand and of carbon monoxide and sulphur on the other show that the same products are formed as when carbonyl sulphide is heated, and that a true case of equilibrium is presented. Similarly, the combustion of carbon disulphide with an insufficiency of oxygen

or of oxygen in carbon disulphide vapour yields a mixture of unchanged carbon disulphide, carbon dioxide, sulphur dioxide, carbonyl sulphide, and carbon monoxide.

The literature of the subject is also critically reviewed.

H. W.

Stabilisation of Dilute Sodium Hypochlorite Solutions (Dakin's Solution). Glenn E. Cullen and Roger S. Hubbard (*J. Biol. Chem.*, 1919, **37**, 511—517).—The regulation of the alkalinity of Dakin's solution may be efficiently carried out either by means of buffer salts or by small amounts of alkali. 0·5% Sodium hypochlorite, prepared by electrolysis of sodium chloride, may be stabilised for use by the addition of 0·5% borax, of 0·5 to 1·0% of sodium carbonate mixtures of p_H 10 to 9·5, or by the addition of 0·2 gram of sodium hydroxide per litre. J. C. D.

Electrolytic Preparation of Dilute Sodium Hypochlorite Solutions (Dakin's Solution). Glenn E. Cullen and Roger S. Hubbard (*J. Biol. Chem.*, 1919, **37**, 519—523).—The influence of temperature on this process was investigated. The optimum point of the curve representing the production of hypochlorite may be raised by raising the initial temperature of the brine. Increase of salt concentration lessens the internal resistance of the cell, and consequently increases the production of sodium hypochlorite per unit of time. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

J. C. D.

The Stability of Javel Extracts. H. Fonzes-Diacon (*Bull. Soc. chim.*, 1919, [iv], **25**, 206—208).—Javel extracts, containing 5 grams of active chlorine per 100 c.c., lose very little of their activity when exposed to light in deep yellow bottles, even after four months. In colourless bottles, the loss is very marked, however, Javel extracts of various strengths tending towards a common limit of about 1 gram of active chlorine per 100 c.c. W. G.

Chemical Decomposition and Electrolytic Formation of Sodium Hyposulphite. K. Jellinek and E. Jellinek (*Zeitsch. physikal. Chem.*, 1919, **93**, 325—367).—The decomposition of sodium hyposulphite has been studied in aqueous solution and in solutions of sodium hydrogen sulphite of various concentrations at the temperatures 0°, 10°, 20°, and 30°. The reaction follows the scheme $2Na_2S_2O_4 = Na_2S_2O_5 + Na_2S_2O_3$; $Na_2S_2O_5 + H_2O = 2NaHSO_3$. The reaction is bimolecular, and the constants have been obtained for the various temperatures. The dependence of the reaction constant on temperature and on the hydrogen sulphite concentration is given by the equation $\log k = A + Bt$, in which A and B are constants. At constant temperature, the reaction constant is proportional to the square of the hydrogen sulphite concentration. The electrolysis of sodium hyposulphite has been investigated, particularly in connexion with the factors which

govern the hyposulphite formation. The electrolysis was carried out with electrodes of various metals, and variable quantities of sulphur dioxide were led into the solution. The concentration of sodium thiosulphate and the amount of hydrogen liberated were measured, and the dependence of these on the time of electrolysis determined. Solutions containing 7—8% of hyposulphite could be obtained. The processes which influenced the current yield were quantitatively explained, and the conditions for obtaining higher yields of hyposulphite indicated. J. F. S.

Cryoscopic Study of Couples. Cadmium Iodide-Alkali Iodide. E. Cornec and G. Urbain (*Bull. Soc. chim.*, 1919, [iv], **25**, 137—142).—For the most part a more detailed account of work already published (compare A., 1914, ii, 428). A cryoscopic study of the couple cadmium iodide–hydrogen iodide in aqueous solution reveals the existence in aqueous solution of the acid salt, $CdI_2,2HI$. W. G.

The Preparation of Cadmium Suboxide. Henry George Denham (T., 1919, **115**, 556—559).

New Preparation of a very Dissociable Calomel. Paul Duret (*Ann. Inst. Pasteur*, 1919, **33**, 174—176).—Calomel may be prepared in a light, voluminous form having a high degree of purity by the following process. A solution containing 6 grams of sodium hydrogen carbonate and 10 grams of dextrose in 80 c.c. of water is added to a solution containing 7·5 grams of crystalline magnesium chloride in 20 c.c. of water, and this mixture is added to a solution containing 11·5 grams of mercuric chloride and ten drops of hydrochloric acid in 100 c.c. of water in a flask. When the reaction has ceased, the mixture is heated on a water-bath until all the carbon dioxide is evolved. The finely divided precipitate of mercurous chloride is then collected and washed with water. In this form it possesses greater germicidal powers than the ordinary preparations when used in prophylactic ointments or anti-syphilitic injections. W. G.

Regeneration of Nessler's Solution. D. Pullman (*Analyst*, 1919, **44**, 124—125).—Residues from the estimation of ammonia by Nessler's method are neutralised and treated with a solution of a soluble mercuric salt in amount equivalent to the iodine present. This precipitates mercuric iodide, which may be washed, dried, and used for the preparation of a modified Nessler's solution. This is made by adding metallic zinc to mercuric iodide suspended in hot water, when the reaction, $Zn + 2HgI_2 = ZnHgI_4 + Hg$, takes place. The zinc mercuric iodide remains in solution, and, after filtration from the mercury, is treated with sodium hydroxide in sufficient quantity to produce the reagent. Experiments have shown that Nessler's reagent thus prepared can replace the ordinary solution containing potassium mercuric iodide. [See also *J. Soc. Chem. Ind.*, 1919, June.] C. A. M.

Mercuric Sulphoxychloride. Sir Prafulla Chandra Rây and Prafulla Kumar Sen (T., 1919, **115**, 552—556).

Manganates and Permanganates. I. Course of the Reaction between Manganese Dioxide, Potassium Hydroxide, and Oxygen, and the Manufacture of Potassium Manganate. H. I. Schlesinger, R. D. Mullinix, and S. Popoff (*J. Ind. Eng. Chem.*, 1919, **11**, 317—323).—When manganese dioxide is heated with potassium hydroxide in a current of air, complete oxidation is frequently attained only by re-moistening and re-heating the mixture. The yield of potassium manganate varies with the proportion of potassium hydroxide present; at about 300°, practically all the manganese dioxide is converted into manganate when two molecules of potassium hydroxide are used for each molecule of manganese dioxide. Mangani-manganates are not formed under these conditions, but larger amounts of potassium hydroxide cause the manganate to decompose into mangani-manganate (compare Sackur, A., 1911, ii, 400). The yield of manganate is lowered when sodium hydroxide is used in place of potassium hydroxide. It is important that the manganese ores used should be powdered as finely as possible. [See, further, *J. Soc. Chem. Ind.*, 1919, 321A.] W. P. S.

Complex Compounds of Tervalent Iron with Hypophosphorous Acid. R. F. Weinland and Walter Hieber (*Ber.*, 1919, **52**, [*B*], 731—741).—In a previous communication (*Zeit. anorg. Chem.*, 1919, **106**) it has been shown that tervalent iron forms a complex cation with hypophosphorous acid, $[Fe_3(H_2PO_2)_6]'''$. It is now established that a similar complex anion can also exist. If the basic ferric hypophosphite, $Fe_3(H_2PO_2)_8{\cdot}OH$, is dissolved in warm concentrated solutions of alkali hypophosphites and the solutions are allowed to evaporate, pale reddish-violet crystals separate having the composition $Fe(H_2PO_2)_3,2K(Na)H_2PO_2,H_2O$. The molecule of water is firmly retained. The properties of these salts lead the authors to ascribe to them the constitution $\left[Fe\begin{matrix}(H_2PO_2)_5\\H_2O\end{matrix}\right]K_2(Na_2)$. When the salts are dissolved in water, a basic ferric hypophosphite is precipitated,

$$3\left[Fe\begin{matrix}(H_2PO_2)_5\\H_2O\end{matrix}\right]K_2=\left[Fe_3\begin{matrix}(H_2PO_2)_6\\OH\end{matrix}\right](H_2PO_2)_2+H_3PO_2+6KH_2PO_2+2H_2O,$$

a complex cation being thus transformed into a complex anion; the latter is only stable in solution in the presence of a large excess of alkali hypophosphite, and the composition of the basic salt varies somewhat.

Since hypophosphorous acid and ferric iron can thus combine to form both complex acid and complex base, it is to be expected that these will combine with one another to yield salts which appear to be ferric hypophosphites. Their constitution follows from their mode of formation. Thus, if concentrated ferric chloride solution

is slowly added to warm concentrated alkali hypophosphite, the ferric hypophosphite formed is immediately dissolved, yielding the complex pentahypophosphito-ion; on continued addition, however, a sudden precipitation occurs, and further precipitations can be obtained from the successive filtrates. These salts are all feebly basic or practically neutral, the composition of which varies between $Fe:H_2PO_2=1:2{\cdot}71$ and $1:2{\cdot}86$. *Salts* are thus obtained containing (i) two hexahypophosphito-cations, one pentahypophosphito-anion, and two hypophosphite radicles; (ii) a similar salt containing three hypophosphite radicles, and (iii) a salt composed of one complex anion and cation. Similarly, when a solution of ferric hypophosphite in hypophosphorous acid (50%) is evaporated over sulphuric acid, a salt is obtained containing one triferrihexahypophosphito-cation and one pentahypophosphito-anion, and either three or four molecules of hypophosphorous acid.

The ability of hypophosphorous acid to yield both complex anions and cations with ferric iron is shared only by formic and salicylic acids; the reason may possibly lie in the somewhat similar structure, $H{\cdot}C\lessdot^{O}_{OH}$ and $H_2{\cdot}P\lessdot^{O}_{OH}$, of formic and hypophosphorous acids. H. W.

The Normal Nitrides of Nickel and Cobalt. A. C. Vournasos (*Compt. rend.*, 1919, **168**, 889—891).—*Nickel nitride*, Ni_3N_2, is readily obtained if a mixture of anhydrous nickelous oxide and anhydrous nickel cyanide in the proportion of $1:0{\cdot}74$ is dropped in small quantities at a time through an arc between two carbon electrodes in an atmosphere of nitrogen, providing the temperature of the arc is near 2000°. The nitride so obtained is not magnetic. It burns in oxygen, giving nickelous oxide and nitrogen peroxide. It is decomposed when heated in chlorine, and also by nitric and hydrochloric acids. It is not decomposed by boiling water.

Cobalt nitride, Co_3N_2, a brown powder, may be similarly prepared, and possesses similar properties. W. G.

Existence of *iso*Tungstic Acid. P. Barbe (*Mon. Sci.*, 1919, [v], **9**, i, 73—75).—Results of a critical research led the author to the opinion that *iso*tungstic acid and ammonium *iso*tungstate do not exist; the ammonium *iso*tungstate described by Gerber (A., 1917, ii, 575) was actually ammonium sodium tungstate. The author has worked for some years on tungsten, and, without going as far as to deny the existence of neotungsten, states that he has never met with a specimen of the metal having a molecular weight higher than usual. [See, further, *J. Soc. Chem. Ind.*, 1919, June.] W. P. S.

Mineralogical Chemistry.

Oruetite, a New Sulphotelluride of Bismuth. S. Piña de Rubies (*Anal. Fís. Quím.*, 1919, **17**, 83—87).—This mineral, discovered in the Serranía de Ronda, in Spain, occurs on dolomite in laminar masses accompanied by scheelite, pyrites, mispickel, limonite, bismuthite, and native bismuth. The laminæ show a brilliant steel-grey, metallic lustre, and are easily exfoliable. Hardness, 1·5—2. Density, 7·6. The resemblance to tetradymite is very marked. The mean of seven analyses gave: Bi 86·78%, Te 6·35%, S 6·84%. This analysis is in agreement with the formula Bi_8TeS_4. A study of the ternary system bismuth–sulphur–tellurium shows the existence of the compounds Bi_2S_3, Bi_2Te_3, and Bi_2Te_3,Bi_2S_3 (Amadori, A., 1918, ii, 366), the naturally occurring sulphotellurides, tetradymite (variety with sulphur), joseite, grünlingite, oruetite, being regarded as eutectic mixtures. The author proposes the following representation of these eutectics: tetradymite (with sulphur), $Bi_2Te_3,Bi_2S_3—Bi_2Te_3$; joseite, $Bi_2Te_3,Bi_2S_3—5Bi$?; grünlingite, $Bi_2Te_3,Bi_2S_3—2Bi_2S_3—4Bi$; oruetite, $Bi_2Te_3,Bi_2S_3—3Bi_2S_3—14Bi$.

W. S. M.

Hydrated Ferric Oxides. Eugen Posnjak and H. E. Merwin (*Amer. J. Sci.*, 1919, [iv], **47**, 311—348).—Analyses of a number of naturally occurring hydrated ferric oxides, from many localities, have been made, and the detailed results given in the paper. Dehydration curves and specific gravities of some of the specimens have been obtained. The experiments show that there is only one hydrate of natural ferric oxide, and this is the monohydrate. The descriptions given in the literature of a series of hydrates ranging from $Fe_2O_3,\frac{1}{2}H_2O$ to $Fe_2O_3,3H_2O$ are therefore erroneous. The monohydrate occurs in nature in two polymorphic forms, goethite and lepidocrocite, and in an amorphous condition, limonite. *Goethite* is orthorhombic, $a:b:c=0·91:1:0·602$, D $4·28\pm0·01$, α 2·26, β 2·394, γ 2·400; it has a dull orange-yellow streak and a faint pleochroism. *Lepidocrocite* is orthorhombic, $a:b:c=0·43:1:0·64$, D $4·09\pm0·04$, α 1·94, β 2·20, γ 2·51; it has a dull orange streak and a very strong pleochroism. *Limonite* is essentially isotropic ferric oxide monohydrate with adsorbed and capillary water. The fibrous mineral *turgite* is variable in composition, and is probably a solid solution of goethite in hæmatite with enclosed and adsorbed water. No definitely crystallised synthetic hydrated ferric oxide has been prepared, and only two types of amorphous hydrated ferric oxide exist, one yellow and the other reddish-brown. The yellow substance is essentially ferric oxide monohydrate, whilst the reddish-brown substance may hold its water either in a dissolved or an absorbed condition, or both. J. F. S.

Turite (= Turgite) and other Iron-Ores from Nova Scotia. L. J. Spencer (*Min. Mag.*, 1919, **18**, 339—348).—The group of ferric hydroxide minerals include the following species (hæmatite being added to complete the series):

		H_2O%.	Sp. gr.
Hæmatite	Fe_2O_3	0·0	5·2
Turite	$2Fe_2O_3,H_2O$	5·3	4·3
Goethite	Fe_2O_3,H_2O	10·1	4·2
Hydrogoethite	$3Fe_2O_3,4H_2O$	13·1	3·7
Limonite	$2Fe_2O_3,3H_2O$	14·5	3·9
Xanthosiderite	$Fe_2O_3,2H_2O$	18·4	—
Limnite	$Fe_2O_3,3H_2O$	25·3	2·8
Esmeraldaite	$Fe_2O_3,4H_2O$	31·1	2·6

Of these, goethite is the only one that occurs as distinct crystals; the remainder have sometimes been regarded as colloids of indefinite composition, and in some of the recent text-books are treated all together under limonite. Turite and limonite possess, however, a fibrous, crystalline structure with definite optical characters, and their dehydration curves are quite distinct from one another and from that of goethite. Turite (the more familiar spelling, turgite, is an incorrect German transliteration from the Russian) usually occurs as a layer on limonite, and forms hard ($H = 6\frac{1}{2}$), lustrous, mamillated or botryoidal masses with a radially-fibrous and concentric-shelly structure. It is black with often a reddish tinge of colour and a brilliant sub-metallic lustre; the streak is dark cherry-red, and very thin fibres transmit a crimson colour. It decrepitates violently when heated.

The other Nova Scotian iron ores include magnetite, hæmatite, chalybite, mesitite, ankerite, and brilliant pseudomorphous crystals of hæmatite after goethite. L. J. S.

The Occurrence of Polyhalite in the Older Zechstein Potassium Salt Deposits in Relation to Van't Hoff's Conclusions. M. Rosza (*Zeitsch. anorg. Chem.*, 1919, **105**, 167—170).—The occurrence of primary and secondary deposits of polyhalite, $Ca_2K_2Mg(SO_4)_4,2H_2O$, is in general agreement with what is to be expected from van't Hoff's work. The salt is met with in almost all potassium-containing parts of the older Zechstein salt deposits, with the exception of the carnallite layers. As a primary deposit, it is found here and there in the "Steinsalz." Elsewhere, as in the kieserite transition zone of the Stassfurt carnallite layer, it is represented by its decomposition products, anhydrite, kieserite, sylvine, and carnallite, formed through the infiltration of liquors rich in magnesium chloride from the carnallite region. Where the carnallite–kieserite layers have undergone hydrothermal change, the conditions may have become favourable for the formation of polyhalite as a secondary deposit. Where hard salt formation has taken place under conditions which would preclude the formation of polyhalite, or where only a purely thermal decomposition of carnallite has occurred, no polyhalite is found. The presence of polyhalite is of great importance from the point of view of chemical genetics. E. H. R.

The Presence of Boron in some Natural Basic Silico-aluminates. A. LACROIX and A. DE GRAMONT (*Compt. rend.*, 1919, **168**, 857—861).—A spectrographic study of three basic silico-aluminates from Madagascar, saphirine, grandidierite, and kornerupine (compare A., 1912, ii, 1182), revealed the presence of boron, and this was confirmed by a further chemical analysis. The boron content of the minerals increased in the order named. The authors consider that boron replaces aluminium isomorphously in these minerals. A number of other silico-aluminates were also examined spectrographically. Boron was found in dumortierite and certain idocrases, whilst in other idocrases its presence was not detected. Similarly, it could not be detected in andalusite, sillimanite, disthene, or in the natural hydrated aluminas examined.

W. G.

Ferrierite, a New Zeolitic Mineral, from British Columbia. R. P. D. GRAHAM (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, Sect. IV, 185—190).—The mineral occurs in veins of chalcedony and calcite in decomposed basalt on the north shore of Kamloops Lake. It forms white, spherical aggregates of colourless, orthorhombic blades with a perfect pearly cleavage parallel to (100), D 2·150, *H* 3—3½, α 1·478, β 1·479, γ 1·482. Analysis of the transparent blades carefully freed from chalcedony gave:

SiO_2.	Al_2O_3.	CaO.	MgO.	Na_2O.	K_2O.	H_2O.	Total.
69·13	11·44	nil	2·92	3·97	0·36	13·05	100·87

corresponding with Clarke's general formula for ptilolite and mordenite, namely, $Al_2(Si_2O_5)_5R'_4+6H_2O$, where R'_2=Mg, Na_2, H_2. Ferrierite, however, differs from all other zeolites in containing magnesium in place of calcium. The mineral commences to lose water at or below 100°; about half is lost at 205°, whilst at 275° 5·71% is still retained, and is probably in part basic.

L. J. S.

Scapolite from the Kiruna District, Swedish Lapland. NILS SUNDIUS (*Akad. Abhandl. Upsala*, 1915, 197—224, and *Vetenskapliga och praktiska undersökningar i Lappland, anordnade av Luossavaara-Kiirunavaara Aktiebolsg*; from *Jahrb. Min.*, 1918, *Ref.* 255—257).—The rocks of this district are rich in scapolites, which are very fresh and form fine-grained masses or large, prismatic aggregates. They have been produced by regional pneumatolytic metamorphism, the chlorine, carbon dioxide, and sulphur trioxide having been introduced by magmatic emanations, whilst the other constituents have been derived from the felspars of the pre-existing rocks. Analysis I is of scapolite from amphibolite at Vahâive, II from greenstone at Pahtosvaara, and III from scapolite-diopside-amphibolite at Kalpivaara.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	Cl.	F.	SO_3.	CO_2.	Sp. gr.
I.	48·52	27·53	0·25	13·31	1·24	—	0·55	n.d.	2·710—2·720
II.	54·82	22·49	—	7·37	3·04	—	0·56	n.d.	2·632
III.	57·31	22·07	—	6·27	3·49	0·02	0·25	0·34	2·610

The relation between the optical constants and the composition of these materials is shown in another paper by the same author (this vol., ii, 163). L. J. S.

Viridine and its Relation to Andalusite. E. A. Wülfing (*Sitzungsber. Heidelberg. Akad. Wiss., Math.-nat. Kl.*, 1917, *Abh.* 12; from *Jahrb. Min.*, 1918, *Ref.* 259—261).—Viridine from Darmstadt (D 3·220) was described by G. Klemm (A., 1913, ii, 423) as a green variety of andalusite containing Fe_2O_3 4·16 and Mn_2O_3 4·77%, the formula being $(Al,Mn,Fe)_2SiO_5$, and a similar mineral (D 3·205) from Vestanå, Sweden, was described by H. Bäckström under the name manganandalusite (A., 1897, ii, 271). These are compared optically with the ordinary type of red andalusite (D 3·154) and with greenish-yellow andalusite from Brazil (D 3·162, which has not been analysed, but is probably similar to the red andalusite). Viridine is optically positive with $\gamma = c$, whilst andalusite is optically negative with $\alpha = c$. On account of this difference, viridine is considered to be distinct from andalusite, and consequently Al_2SiO_5 is regarded as tetramorphous, as represented by the minerals kyanite, sillimanite, andalusite, and viridine. L. J. S.

The Pelham Asbestos Mine, Massachusetts. Earl V. Shannon (*Amer. Min.*, 1919, **4**, 37—39).—Various minerals are developed at the junction of an intrusive mass of peridotite (saxonite) in acid gneiss at this locality. The outer portion of the saxonite is changed to fibrous anthophyllite, which is here mined as asbestos. Associated with biotite is a saponaceous, silvery, bluish-green mineral composed of fine scales; on drying, it becomes opaque and pale olive-green. Analyses I and II of material slightly contaminated with biotite and actinolite prove that this is the "pelhamite" of J. P. Cooke (1875), which is classed by Dana as a vermiculite.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	H_2O $<105°$.	H_2O $>105°$.	Total.
I.	40·08	21·65	3·59	0·58	20·12	3·79	7·83	97·64
II.	38·88	19·27	3·99	—	22·66	3·36	9·54	97·90

L. J. S.

The Origin of Septarian Structure. W. Alfred Richardson (*Min. Mag.*, 1919, **18**, 327—337).—The origin of the system of polygonal cracks in septarian nodules is discussed in detail. The expansion and contraction theories are dismissed, and it is concluded that the cracks are due to the desiccation of a colloidal centre by chemical means. Similar structures are produced artificially when pats of clay are air-dried or immersed in a concentrated solution of calcium chloride. The following partial analyses are of I*a*, the exterior portion, and I*b*, the central portion, of an ironstone septarium from the Lias at Bracebridge, Lincolnshire, and II of the clay in which the nodules are embedded.

III of a limestone septarium from Nottinghamshire, *a* the exterior, *b* 1 inch from the outside, and *c* the centre.

	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.
I*a*.	24·7	18·6	34·3	—
I*b*.	13·1	35·1	4·7	22·9
II.	53·1	31·1	7·3	—
III*a*.	12·3	trace	7·2	36·3
III*b*.	8·0	2·0	3·9	45·3
III*c*.	4·5	4·0	3·5	46·0

The nodules probably originated by the rhythmic precipitation of solutions diffusing through a colloid according to Liesegang's laws. L. J. S.

Analytical Chemistry.

A Simplification of the McLean-van Slyke Method for Estimation of Plasma Chlorides. Donald D. van Slyke and John J. Donleavy (*J. Biol. Chem.*, 1919, **37**, 551—555).—The method previously described (A., 1915, ii, 573) has been simplified by reducing the number of filtrations necessary. The standard silver nitrate solution is made up to contain, in addition to the nitrate, 7·5 grams of picric acid per litre. This solution precipitates both protein and chlorides simultaneously. The excess of silver in the filtrate is titrated with potassium iodide. J. C. D.

Indirect Electrolytic Estimation of Anions without Platinum Electrodes. E. Lasala (*Anal. Fis. Quim.*, 1919, **17**, 88—95).—The present preliminary investigation is concerned with the estimation of chloride, bromide, and iodide. The halogen is precipitated as silver haloid by means of a 5% solution of silver nitrate. The precipitate is filtered through glass wool and dissolved in 20% solution of potassium cyanide to which a little sodium hydroxide is added. The solution is electrolysed with a nickel-plated copper cathode and a rotating iron anode. Towards the end of the electrolysis, the electrolyte is heated nearly to boiling. The results are most satisfactory. The cathode is prepared by electrolysis of an ammoniacal solution of nickel sulphate. W. S. M.

Iodometric Studies. The Starch-Iodine Reaction. I. M. Kolthoff (*Pharm. Weekblad*, 1919, **56**, 391—404).—A systematic investigation of the sensitiveness of the starch–iodine reaction under varying conditions. The sensitiveness is increased by the presence of salts, especially potassium iodide, and acids (A., 1895, i, 79). Increased temperatures and presence of organic substances

such as alcohols, albumin, etc., diminish the sensitiveness. The magnitude of the correction to be applied in the titration of dilute iodine solutions with dilute thiosulphate solutions, and vice versâ, was determined. The correction is a minimum in hydrochloric acid solution to which a little potassium iodide has been added.

W. S. M.

The Iodometric Estimation of Bromate (and Iodate). I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 426—438).—In the titration with thiosulphate solution of bromate solutions to which potassium iodide has been added, the concentrations of bromate and iodide are factors of little importance. It is essential, however, that sufficient acid be present in the mixture. The minimum concentration required in the solution is 0·5*N* for hydrochloric acid and about 1·0*N* for sulphuric acid if titration is carried out immediately after the addition of the iodide. If too little acid is present, oxidation of the thiosulphate directly to sulphate takes place: $8HBrO_3 + 5H_2S_2O_3 + H_2O = 10H_2SO_4 + 4Br_2$ or $4HBrO_3 + 3H_2S_2O_3 + 3H_2O = 6H_2SO_4 + 4HBr$. In either case, too little of the thiosulphate solution is required. The error may be avoided by allowing the mixture to remain some time before titration, or by the addition of a catalyst. The best catalyst is ammonium molybdate in both strong and weakly acid solutions. The catalytic effect of ferrous sulphate and potassium dichromate is negligible in strongly acid solutions, but is more marked in weakly acid solutions. Light has a positive catalytic effect. Salts such as sodium chloride and sodium sulphate retard the reaction.

The reaction between iodate and iodide is much more rapid than that between bromate and iodide, and therefore the iodometric estimation of iodates is not attended by the difficulties arising in the latter case.

W. S. M.

A Simple Form of Apparatus for Estimating the Oxygen Content of Air from the Upper Atmosphere. FRANCIS WILLIAM ASTON (T., 1919, **115**, 472—475).

Sodium Pyrogalloxide Solution as an Absorbent for Oxygen. G. W. JONES and M. H. MEIGHAN (*J. Ind. Eng. Chem.*, 1919, **11**, 311—316).—The rate of oxygen absorption in sodium pyrogalloxide solutions increases with the dilution of the sodium hydroxide; for any given concentration of sodium hydroxide, the rate of absorption is proportional to the concentration of the pyrogallol. Carbon monoxide is evolved from the solution if the sodium hydroxide solution used has a specific gravity of less than 1·30; all sodium pyrogalloxide solutions evolve carbon monoxide if the sample under examination contains more than 95% of oxygen. A reagent which evolves the minimum quantity of carbon monoxide and has a fairly high rate of absorption is made by dissolving sodium hydroxide in its own weight of water and adding five parts

of this solution to two parts of a solution containing 1 gram of pyrogallol in 3 c.c. of water. W. P. S.

The Relation between the Oxygen Concentration and Rate of Reduction of Methylene-blue by Milk. E. NEWTON HARVEY (*J. Gen. Physiol.*, 1919, **1**, 415—419).—The rate of reduction and decolorisation of methylene-blue by milk in the presence of an aldehyde is proportional to the oxygen concentration. It is suggested that this fact might be made the basis of a method for determining the oxygen content of gaseous mixtures. Carbon dioxide present in concentrations up to 5% does not affect the reducing action of the milk. J. C. D.

Method for the Identification of Sulphur-Oxygen Compounds. A. SANDER (*Chem. Zeit.*, 1919, **43**, 173. Compare A., 1915, ii, 161).—Sulphates, sulphites, hydrogen sulphites, thiosulphates, sulphides, and polythionates may be identified by their different behaviour towards mercuric chloride, this reagent also serving, to a certain extent, for the identification of the compounds in the presence of each other. The following reactions result when the compounds are treated with an excess of mercuric chloride solution: *Sodium Sulphate.*—Mercuric sulphate and sodium chloride are formed, and the solution remains neutral in reaction. *Sodium Sulphite.*—The solution remains clear and is alkaline towards methyl-orange before and after the addition of mercuric chloride; when the mixture is boiled, it becomes acid and calomel is precipitated. *Sodium Hydrogen Sulphite.*—No precipitate; boiling produces a precipitate and the mixture remains acid. *Sodium Sulphide.*—A black precipitate, which rapidly becomes white owing to the formation of a sulphochloride; the mixture has a neutral reaction before and after boiling. *Sodium Thiosulphate.*—As in the case of a sulphide, a white precipitate forms, but the mixture becomes strongly acid; it remains acid when boiled. *Sodium Polythionate.*—Behaves like sodium thiosulphate towards mercuric chloride, but may be distinguished from the latter in that it does not decolorise iodine solution and does not give a precipitate of sulphur when acidified. Sulphite and polythionate cannot exist together in the same solution.

W. P. S.

Volumetric Estimation of Sulphurous Acid. THOS. J. I. CRAIG (*J. Soc. Chem. Ind.*, 1919, **38**, 96T).—The sulphurous acid solution is added to a known excess of hydrogen peroxide solution acidified with dilute sulphuric acid, and the excess of hydrogen peroxide is then titrated with standardised potassium permanganate solution. The reaction proceeds according to the equations $SO_2 + H_2O_2 = H_2SO_4$. and $5H_2O_2 + 2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$. The method may also be applied to solutions containing sulphites or hydrogen sulphites. W. P. S.

Estimation of Total Nitrogen, including Nitric Nitrogen [in Soil Extracts]. B. S. Davisson and J. T. Parsons (*J. Ind. Eng. Chem.*, 1919, **11**, 306—311).—The method recommended consists in boiling the soil extract solution with a quantity of sodium hydroxide sufficient to make the alkalinity approximately *N*/10, reduction of the nitric nitrogen being effected by the addition of Devada's alloy. The boiling flask is connected with an absorption tube containing an excess of sulphuric acid (4:1). The contents of the absorption tube are then washed into the flask, the mixture is evaporated until charring commences, potassium sulphate is added, and the digestion continued. The ammonia formed is distilled after the addition of sodium hydroxide and sodium sulphide. [See, further, *J. Soc. Chem. Ind.*, 1919, 332A.]

W. P. S.

Estimation of Nitrous Acid and Nitrites. J. S. Laird and T. C. Simpson (*J. Amer. Chem. Soc.*, 1919, **41**, 524—531).—The volumetric methods for the estimation of nitrous acid and nitrites, as described in the literature, have been experimentally examined and shown to be unsatisfactory. The authors have devised a method for estimating nitrites which consists in the oxidation of the nitrite in acid solution with excess of potassium permanganate, reduction of the excess of permanganate by an excess of ferrous sulphate, sodium oxalate, or hydrogen peroxide, and titration of the excess of the reducing agent by permanganate. In the actual estimation, the nitrite is run slowly into the excess of permanganate, acidified with 1:4-sulphuric acid, and constantly shaken. The titration is not interfered with by moderate amounts of chloride or small amounts of bromide. Silver nitrite is not a satisfactory material for use as a standard in nitrite estimations. A satisfactory standard solution may be made by titrating sodium nitrite solution with potassium permanganate according to the method described above, or sodium nitrite solution may be standardised gravimetrically by the reduction of silver bromate to silver bromide according to Busvold's method (A., 1914, ii, 144).

J. F. S.

Gravimetric Estimation of Phosphoric Acid as Magnesium Pyrophosphate. Z. Karaoglanow (*Zeitsch. anal. Chem.*, 1918, **57**, 497—541).—An investigation of the different methods employed for the precipitation of phosphoric acid as ammonium magnesium phosphate previous to the conversion of the precipitate into magnesium pyrophosphate. To a slight extent, the precipitation depends on temperature, rate of precipitation, and presence of varying quantities of magnesium chloride, ammonium chloride, etc.: the differences in the final results are usually very small. The lack of a more trustworthy method for the estimation of phosphoric acid and the difficulty of obtaining a substance of known phosphorus content render it impossible to say which method of precipitation gives the true quantity of phosphoric acid present.

W. P. S.

Gravimetric Analysis. X. XII. Estimation of Phosphoric Acid. L. W. Winkler (*Zeitsch. angew. Chem.*, 1919, **32**, 98—101).—Precipitation of phosphoric acid as ammonium magnesium phosphate and weighing it as such or after ignition to magnesium pyrophosphate, yields trustworthy results. The presence of large quantities of potassium and sodium chlorides does not influence the results when the precipitate is weighed in the form of ammonium magnesium phosphate, but when the precipitate is converted into pyrophosphate, the result is too high if potassium chloride was present in the solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 391A.] W. P. S.

Estimation of Arsenic in Volatile Cacodyl Compounds. L. C. Maillard (*Bull. Soc. chim.*, 1919, [iv], **25**, 192—200).—The method is based on the oxidation of the cacodyl compound to cacodylic acid, and subsequently to arsenic acid. The arsenic is then separated in the usual manner by precipitation as magnesium ammonium arsenate, and weighed as pyroarsenate. For the first stage of the oxidation, a suitable weight of the cacodyl compound, in a sealed bulb if liquid or in a narrow tube if solid, is introduced into a flask containing 3 grams of ammonium persulphate, 30 c.c. of water, and 10 c.c. of sulphuric acid. The flask is quickly closed with a ground-in stopper and thoroughly shaken until the air in the flask, at first cloudy, is quite clear. Ten c.c. of fuming nitric acid are now added, and the estimation proceeded with in the usual way, the arsenic being first precipitated as its sulphide if necessary and then redissolved before finally precipitating it as the double arsenate. The method was applied to cacodyl chloride, and found to be simple and accurate. W. G.

Gravimetric Analysis. XI. XIII. Estimation of Arsenic Acid. L. W. Winkler (*Zeitsch. angew. Chem.*, 1919, **32**, 122—124).—Two methods are described for the estimation of arsenic acid. In the first, the arsenic acid is treated with potassium thiocyanate, then with hydrogen sulphide, and the precipitate, consisting of arsenic trisulphide and sulphur, is collected, dried at 100°, and weighed: $As_2O_5 + 2KCNS = 2KOCN + As_2O_3 + S_2$; $As_2O_3 + 3H_2S = As_2S_3 + 3H_2O$. The second method consists in the precipitation of the arsenic acid as ammonium magnesium arsenate; details of the procedure are given in full. Arsenious acid solutions may be oxidised by hydrogen peroxide in the presence of ammonia, and the arsenic then precipitated as ammonium magnesium arsenate. [See, further, *J. Soc. Chem. Ind.*, 1919, June.] W. P. S.

Selection of an Indicator for the Acidimetric Estimation of Boric Acid. Johannes Prescher (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 283—286).—Phenolphthalein is considered to be the most suitable indicator for the purpose. W. P. S.

Electrical Precipitator for Analysing Smokes. Richard C. Tolman, L. H. Reyerson, A. P. Brooks, and H. D. Smyth (*J. Amer. Chem. Soc.*, 1919, **41**, 587—589).—A modified form of the Cottrell precipitator is described which has been used for removing the solid particles from smokes. The apparatus consists of a glass tube 1·6 cm. in diameter and 25 cm. long, a thin aluminium foil cylinder 0·025 mm. thick is placed in the glass tube and constitutes the anode, and a cathode consisting of a No. 25 platinum wire threaded with a jeweller's die passes centrally down the aluminium cylinder. Entrance and exit tubes for the smoke are attached at the ends. A high-voltage circuit (15,000 volts) is attached to the electrodes, and a corona discharge produced; sparking must be avoided. The smoke is then admitted at the rate of 5 litres per minute, when the negatively charged particles are deposited on the aluminium foil. The weight of particles is determined by weighing the anode before and after the precipitation. J. F. S.

Characterisation and Estimation of Carbonyl Chloride. André Kling and René Schmutz (*Compt. rend.*, 1919, **168**, 773—775).—Carbonyl chloride readily reacts with an excess of aniline in saturated aqueous solution to give diphenylcarbamide and aniline hydrochloride. Thus a trace of carbonyl chloride in air may readily be detected by bubbling 5 litres of the air at the rate of 1 litre in five minutes through the aqueous solution of aniline, and characterising the precipitate microscopically and by its m. p. as diphenylcarbamide, which is practically insoluble in water. By this means, carbonyl chloride may be detected in the air at a dilution of 1 in 100,000. For the estimation of carbonyl chloride in solution in organic solvents, a quantity of the solution containing 0·2—0·35 gram of carbonyl chloride is added to 150 c.c. of the aqueous aniline solution (containing 26 grams of aniline per litre), and after two hours the mixture is heated on a water-bath for one hour to drive off the organic solvent. The liquid is allowed to cool, and the next day the precipitate of diphenylcarbamide is collected on a Gooch crucible, dried at 70°, and weighed. W. G.

Estimation of Traces of Carbonyl Chloride in Air. André Kling and René Schmutz (*Compt. rend.*, 1919, **168**, 891—893).—Using the method previously described (preceding abstract), the carbonyl chloride may be estimated gravimetrically if the weight of diphenylcarbamide exceeds 10 mg. by dissolving the precipitate off the filter with alcohol and evaporating the alcoholic solution in a weighed platinum crucible at a temperature not exceeding 60°, after which the residue is dried at this temperature for two hours. Alternatively, a colorimetric method may be employed by digesting the precipitate and filter paper with sulphuric acid and mercuric sulphate, and proceeding as in the ordinary Kjeldahl process, the ammonia passing over being collected in *N*/250-hydrochloric acid, and finally estimated by means of Nessler's reagent. W. G.

Analyses of Mixtures of Vapours containing Carbon Monoxide, Carbon Dioxide, Carbonyl Sulphide and Carbon Disulphide and similar Mixtures of Gases. ALFRED STOCK and PAUL SEELIG (*Ber.*, 1919, **52**, [*B*], 672—680. Compare Stock and Kuss, A., 1917, ii, 205).—The processes described depend on the difference in the rates with which the various gases or vapours are absorbed by alkali.

Carbon dioxide is immediately absorbed by alkali hydroxides of widely differing concentrations. Carbonyl sulphide is absorbed by the hydroxides of rubidium, potassium, sodium, and lithium in order of decreasing rapidity; with sodium hydroxide, the rate of absorption varies with the concentration, being at a minimum with a 30% solution; the gas is completely absorbed in about an hour. The complete absorption of carbon disulphide vapour by aqueous alkali hydroxide requires several days, whilst carbon monoxide is not absorbed.

An alternative method of estimating carbon disulphide in gaseous mixtures, which can be rapidly and accurately performed, consists in saturating a measured volume of the gas with carbon disulphide and measuring the increase in volume.

Two methods are described for the analysis of the mixture. (1) A measured volume of the gas is shaken with sodium hydroxide solution (30%, 1 c.c.), and the volume read off each minute during several minutes (CO_2). Water (4 c.c.) is now added, and the gas volume is determined every ten minutes for about an hour (COS). Potassium hydroxide (30%, 1 c.c.) is now added, and the volume recorded after one, two, three, etc., days (CS_2). The residue is carbon monoxide, which must be completely absorbed by cuprous chloride solution. (2) Carbon dioxide is estimated in one portion as usual. A second portion is intermittently shaken with sodium hydroxide (2—3 c.c., 50%); after fifteen to thirty minutes, shaking is made continuous, and the volume read off each minute until it is constant ($CO_2 + COS$). A third portion is shaken occasionally with potassium hydroxide (5%, 2—3 c.c.), and the volume determined daily until constant ($CO_2 + COS + CS_2$), the residual carbon monoxide being tested for purity by means of ammoniacal cuprous chloride solution. Alternatively, the residue obtained after absorption of CO_2 and COS may be saturated with carbon disulphide and the increase in volume determined.

The paper also contains a vapour tension–temperature table for aqueous sodium hydroxide solutions of differing concentration and for carbon disulphide, for which the data given in the literature are somewhat discordant. H. W.

Estimation of Alkali in Permanganate Liquors. THOS. J. I. CRAIG (*J. Soc. Chem. Ind.*, 1919, **38**, 96—97T).—The method depends on the reaction between permanganate and hydrogen peroxide, $5H_2O_2 + 2KMnO_4 = 2KOH + 2MnO_2 + 4H_2O + 4O_2$. After filtration, the alkalinity is estimated by titration; the alkalinity due to the permanganate is deducted from the result, and the

remainder represents the quantity of free alkali (hydroxide or carbonate) in the solution. With manganates, the reaction proceeds according to the equation $H_2O_2 + Na_2MnO_4 = 2NaOH + MnO_2 + O_2$. In analysing mixtures containing both permanganate and manganate, the proportions of these compounds may be found by treating a portion of the solution with carbon dioxide or sodium hydrogen carbonate to convert the manganate into permanganate, $3Na_2MnO_4 + 2CO_2 = 2NaMnO_4 + 2Na_2CO_3 + MnO_2$; the precipitated manganese dioxide (which contains manganese equivalent to one-third of the manganate) is collected, and its quantity estimated by titration with ferrous sulphate and permanganate solutions.

W. P. S.

Conditions affecting the Precise Estimation of Zinc as the Sulphide. HAROLD A. FALES and GERTRUDE M. WARE (*J. Amer. Chem. Soc.*, 1919, **41**, 487—499).—The conditions affecting the quantitative estimation of zinc as sulphide have been investigated. It is shown that a hydrion concentration lying between 10^{-2} and $10^{-3}N$ is most favourable for the quantitative precipitation of zinc sulphide in a form suitable for rapid filtration and washing. The concentration of the hydrion may be kept within this range by the use of ammonium citrate or a mixture of ammonium sulphate, ammonium formate, and formic acid. The precipitation of granular zinc sulphide is favoured, not only by a concentration of hydrion within the above-mentioned limits, but also by a high concentration of an ammonium salt of a strong acid, by a concentration of 1 gram of zinc per litre of solution, and by a temperature of 95—100°. It is desirable that the hydrogen sulphide should be passed in under pressure for the purpose of obtaining rapid saturation and avoiding loss of formic acid by evaporation. The authors recommend the following method of procedure. The zinc solution, which has been freed from cadmium, copper, and other elements likely to be precipitated, is evaporated to 125 c.c. and treated with ammonium hydroxide until the precipitate at first formed fails to redissolve, 25 c.c. of a citrate solution (200 grams of citric acid per litre of water neutralised by 15*N*-ammonia) are added, and the whole solution is made neutral to methyl-orange with ammonia. Then 25 c.c. of formic acid mixture (30 c.c. of 15*N*-ammonium hydroxide, 200 c.c. of 13·6*N*-formic acid and 250 grams of ammonium sulphate in 1000 c.c. of water) are added, and the whole is made up to 200 c.c. The solution is heated to 60° and connected with a hydrogen sulphide generator, so that air is slowly expelled from the flask as the heating is continued. At 90—100°, the flask exit is closed, and the solution as it cools saturated with hydrogen sulphide under increasing pressure. The flask should be shaken frequently to ensure saturation, which is usually complete when the precipitate settles rapidly. The precipitate is filtered and washed with a cold 0·1*N*-solution of formic acid saturated with hydrogen sulphide. The precipitate is transferred to a weighed porcelain crucible and

the filter paper charred. The completion of the ignition of the filter paper should be carried out in an oxidising atmosphere, and the reaction should proceed so that the sulphide is converted into sulphate and not into oxide. After cooling, the precipitate is moistened with concentrated sulphuric acid and heated in an air bath until the excess of acid is expelled, and then heated over a flame to remove any charred material. The mass is again moistened with sulphuric acid and heated in the air to expel the excess of acid, allowed to cool in a desiccator, and weighed. The last process is repeated until a constant weight is obtained. A modification of the above process is described which enables zinc to be quantitatively separated from iron, manganese, nickel, and cobalt. The processes described are accurate to one part per thousand. J. F. S.

Separation of Lead in Metallic Calcium and "Lurgie" Metal. J. König (*Chem. Zeit.*, 1919, **43**, 135).—The metal is dissolved in nitric acid, the solution neutralised with ammonia, treated with an excess of bromine-water, then rendered ammoniacal, cooled, and filtered. The lead is thus removed completely, and the calcium may be estimated in the filtrate by precipitation as oxalate. In the case of "lurgie" metal, barium must be separated as sulphate before the calcium is precipitated. [See, further, *J. Soc. Chem. Ind.*, 1919, 370A.] W. P. S.

The Electrolytic Estimation of Mercury without Platinum Electrodes. J. Guzmán and P. Poch (*Anal. Fis. Quim.*, 1918, **16**, 742—755).—*Estimation in Nitric Acid Solution.*—A copper cathode and a graphite anode are used. The cathode is plated with a brilliant deposit of silver from cyanide solution, and is then washed successively in boiling water, alcohol, and ether. The mercury solution must be only slightly acid, and in order to preserve the anode, the voltage must not exceed three volts. The electrolysis is carried out in the cold. By this method, results with a maximum error of 0·3% are obtained. A similar procedure with mercuric chloride solution gives results which are less satisfactory. Excellent results are obtained with the silvered cathode and a fine platinum spiral as anode, and also with a copper cathode plated with copper by electrolysis in copper sulphate solution acidified with nitric acid. The presence of the chlorine ion is detrimental. The copper cathode may be used seven or eight times, but after every analysis the mercury must be removed by heating, and the silver with cyanide solution.

Estimation in Ammoniacal Solution.—The anode is of iron which has been heated to redness and allowed to cool in the air. A voltage of 2·4 volts is employed. The copper cathode is first nickel-plated and then covered with a deposit of silver. It is found that, after the first analysis, the employment of the same cathode, even after re-plating, gives results which are no longer quantitative, as the mercury forms a grey powder on washing with

alcohol. The same difficulty is found with cathodes on which had been deposited protective layers of gold, tin, or bismuth. The only cathode which can be used repeatedly is of copper with a deposit of mercury from electrolysis in mercuric nitrate solution. The deposit must be polished by brushing after each determination. The electrolysis is carried out in mercuric nitrate solution to which has been added ammonium nitrate and concentrated ammonia solution. The method is accurate within 0·3%.

Estimation in Alkaline Cyanide Solution.—In this case, the cathode is of copper with a brilliant deposit of silver, and the anode of iron. Sodium hydroxide solution in excess is added to a mercuric nitrate solution, and then just sufficient potassium cyanide to dissolve the precipitate formed. This electrolyte is maintained at 50° during the electrolysis. Voltage, 2·5 volts. The maximum error observed is less than 0·2%. Satisfactory results are obtained by this method in presence of the chlorine ion if the iron anode is replaced by graphite. The method is applicable to the analysis of commercial products containing mercury.

Estimation in Alkaline Sulphide Solution.—The electrolyte is prepared by dissolving precipitated mercuric sulphide in sodium sulphide solution and adding sodium hydroxide solution. With a cathode of amalgamated copper and an anode of iron, the results are moderately satisfactory, but the cathode cannot be used for a repetition of the analysis even after brushing. The addition of potassium cyanide and carbamide to the electrolyte does not lead to any marked improvement in the results. W. S. M.

Gravimetric and Volumetric Estimation of Mercury Precipitated as Mercury Zinc Thiocyanate. George S. Jamieson (*J. Ind. Eng. Chem.*, 1919, **11**, 296—297).—A solution of a mercuric salt or compound (containing about 0·14 gram of mercury) is treated with 25 c.c. of a solution containing 39 grams of ammonium thiocyanate and 29 grams of zinc sulphate per litre. The precipitate of mercury zinc thiocyanate formed is collected, washed with a solution prepared by diluting 5 c.c. of the thiocyanate reagent with 450 c.c. of water, dried at 105°, and weighed. The weight of the precipitate is multiplied by 0·40258 to obtain the quantity of mercury present. The volumetric method consists in treating the moist precipitate with 35 c.c. of concentrated hydrochloric acid, 10 c.c. of water, and 7 c.c. of chloroform, and titrating the mixture with standardised potassium iodate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 341A.] W. P. S.

Estimation of Uranium in Alloy Steels and Ferrouranium. G. L. Kelley, F. B. Meyers, and C. B. Illingworth (*J. Ind. Eng. Chem.*, 1919, **11**, 316—317).—The sample is dissolved in hydrochloric acid, nitric acid is added, and silica and tungstic acid are separated; the greater part of the ferric chloride is then removed by extraction with ether, the solution is boiled with the addition of an excess of sodium carbonate, and filtered.

The filtrate, containing the uranium together with molybdenum and vanadium, is acidified with sulphuric acid, boiled, rendered ammoniacal, and again boiled. Uranium and some vanadium are precipitated; the precipitate is heated with ammonium carbonate solution, the mixture filtered to remove traces of manganese, iron, etc., and the filtrate acidified with sulphuric acid, boiled, and the uranium and vanadium reprecipitated by ammonia. The precipitate is collected, ignited, and weighed. The small quantity of vanadium it contains is estimated by titration with permanganate solution after solution in hydrochloric acid, or by oxidation with ammonium persulphate and silver nitrate, followed by electrometric titration. [See, further, *J. Soc. Chem. Ind.*, 1919, June.]

W. P. S.

Analysis of Natural Gas and the Calculation and Application of Results. R. P. Anderson (*J. Ind. Eng. Chem.*, 1919, **11**, 299—306).—An indicator is described for showing complete combustion of the sample when the natural gas is passed slowly into oxygen in which an electrically heated platinum spiral is glowing; this indicator consists of a narrow glass tube connected by means of a T-piece with the rubber tubing connecting the combustion pipette with the levelling bulb; when the gas has been passed into the pipette, the tap on the levelling bulb is closed, and the contractions of the gases in the pipette are shown by the fall of the level of mercury in the narrow tube. When this fall ceases, combustion is complete. The combustion pipettes should be made of Pyrex glass. Calculation of results of combustions of natural gas according to theoretical equations is discussed, and tables of correction factors are given. W. P. S.

Detection of Methyl Alcohol. E. Salkowski (*Zeitsch. Nahr. Genussm.*, 1918, **36**, 262—270).—Tests which depend on the oxidation of the methyl alcohol by potassium permanganate and on the detection of the formaldehyde produced are fairly trustworthy when applied to mixtures of methyl alcohol and pure ethyl alcohol, since the latter does not yield formaldehyde. Higher alcohols (propyl, *iso*butyl, and *iso*amyl), however, yield distinct quantities of formaldehyde when oxidised by permanganate; the colorations obtained are less intense than those yielded by methyl alcohol, and the tests may be used, with due caution, for the detection of methyl alcohol in ethyl alcohol. Only small quantities of higher alcohols are likely to be present in commercial alcohol, whilst alcohol deliberately adulterated with methyl alcohol usually contains not less than 10% of the latter. [See, further, *J. Soc. Chem. Ind.*, 1919, 382A.] W. P. S.

[A Case of Poisoning by Methyl Alcohol and] a Simple Method of Distinguishing between Methyl Alcohol and Absolute Ethyl Alcohol or Spirit. Th. Sabalitschka (*Ber. Deut. pharm. Ges.*, 1919, **29**, 214—219).—In connexion with a

case of poisoning due to the substitution of methyl alcohol for ethyl alcohol, the author has elaborated the following method for distinguishing between these substances. The specimen (2 c.c.) is frequently shaken during ten minutes with powdered crystalline copper sulphate (0·1 gram), and the solution is filtered. The filtrate is treated with water (5 c.c.) and ammonia solution (10%, 3 c.c.); with methyl alcohol, a deep blue to blue coloration is developed, whilst with ethyl alcohol the solution is only coloured a faint, pale blue. The method may also be used to obtain an approximate estimation of methyl alcohol in mixtures of the latter with absolute alcohol, providing the content is not less than 20%; if this is the case, the specimen must be distilled and the test performed on the first portion of the distillate. In the presence of water, even in small quantities, the process is useless, since the solutions of hydrated salts in alcohol are unstable, and the presence of water promotes separation of the salt.

Copper sulphate may also be replaced by crystalline ferrous sulphate. In this case, separation of the salt occurs with greater readiness, and the sample should only be shaken with the sulphate for five minutes. The presence of iron in the filtrate is detected by addition of water (5 c.c.) and 2·5% potassium ferricyanide solution (2 c.c.), the colorations obtained ranging from dark blue with methyl alcohol to pale green with ethyl alcohol. H. W.

Estimation of Ethyl Ether in Blood. J. W. Le Heux (*Zeitsch. physiol. Chem.*, 1919, **104**, 137—140).—The method of Nicloux ("Les Anesthésiques Généraux," Paris, 1908) has been modified so as to increase the accuracy. Ten c.c. of blood are mixed with 65 c.c. of a saturated solution of picric acid, and the ethyl ether removed by distillation. The ether in the distillate is quantitatively oxidised to acetic acid by chromic acid, and the excess of chromic acid determined by the iodometric method. J. C. D.

A New Method for Estimating small amounts of Dichloroethyl Sulphide (Mustard Gas). E. F. Hopkins (*J. Pharm. Expt. Ther.*, 1919, **12**, 393—403).—See this vol., i, 250.

Estimation of the Different Constituents of a Mixture containing Eugenol, Triacetin, and Benzyl Alcohol. H. Perperot (*Ann. Chim. anal.*, 1919, [ii], **1**, 112—114).—The quantity of triacetin is calculated from the saponification number of the mixture, whilst the iodine number is a measure of the amount of eugenol present. A portion of the mixture is also acetylated in the usual way, and the saponification number of the acetylated product is estimated; after deducting the amount due to triacetin and acetylated eugenol, the remainder is a measure of the acetylated benzyl alcohol. [See, further, *J. Soc. Chem. Ind.*, 1919, 387A.] W. P. S.

Estimation of Thymol. E. Moles and M. Marquina (*Anal. Fís. Quím.*, 1919, **17**, 59—83).—See this vol., i, 270.

Estimation of small Quantities of Acetone, Alcohol, and Benzene in Air. S. Elliott and J. Dalton (*Analyst*, 1919, **44**, 132—136).—The air under examination is aspirated through four absorption cylinders fitted with Folin tubes (*J. Biol. Chem.*, 1912, **11**, 493) connected by means of long rubber tubing with siphon bottles. For the estimation of acetone, one of the absorption vessels is charged with standard iodine and sodium hydroxide solutions, and the excess of iodine subsequently titrated, as in Messinger's method (A., 1889, 313). No appreciable amount of iodoform is formed by the alcohol vapour in the air if the temperature is kept low. Alcohol is estimated by Szeberényi's method (A., 1915, ii, 292) of oxidising it to acetic acid by means of a mixture of potassium dichromate and dilute sulphuric acid, whilst Pfeiffer's method (A., 1904, ii, 786), in which the benzene is nitrated by means of a mixture of nitric and sulphuric acids, gives trustworthy results. In this case, the fourth absorption vessel is charged with sodium hydroxide solution and interposed between the acid absorption vessel and the siphons to protect the tubing. The minimum and maximum amounts of these substances per million c.c. found in the air of factories were: acetone, 0·02 to 1·86 grams, whilst the mean amount found was 0·31 gram; alcohol, 0·02 to 3·00, with a mean of 0·65 gram; benzene, 0·01 to 0·90, with a mean of 0·26 gram. [See also *J. Soc. Chem. Ind.*, 1919, 342A.] C. A. M.

Application of the Grimbert-Leclère Reaction of *apo*-Morphine to Alkaloids and Adrenaline. G. Denigès (*J. Pharm. Bordeaux*, 1918, **56**, 185; from *J. Pharm. Chim.*, 1919, [vii], **19**, 49).—The reaction described by Grimbert and Leclère (A., 1915, ii, 192) is also given by morphine under the following conditions. A few mg. of the alkaloid are heated with 2 drops of sulphuric acid until a slight brown coloration appears; the mixture is then diluted with 5 c.c. of saturated sodium acetate solution, 2 drops of 4% mercuric chloride solution are added, and the mixture is boiled. A green coloration is obtained. Catechol, when boiled with sodium acetate and mercuric chloride, yields a reddish-violet substance, which is soluble in ether, chloroform, and amyl alcohol. Adrenaline, treated similarly, but not heated above 50°, gives a red coloration; the reaction may be obtained with as little as 0·01 mg. of adrenaline. W. P. S.

Estimation of the Non-Protein Nitrogenous Constituents of Milk. W. Denis and A. S. Minot (*J. Biol. Chem.*, 1919, **37**, 353—366).—For the estimation of total non-protein nitrogen in cows' milk, the protein and fat are removed by heating in the presence of copper sulphate. The filtrate is treated with formaldehyde, which prevents the precipitation of amino-acids as insoluble copper compounds during the subsequent removal of the lactose with cupric hydroxide. For the latter process, calcium hydroxide is preferred to sodium hydroxide, as any excess of calcium may be removed as oxalate. The total nitrogen is

estimated by conversion into ammonia with subsequent Nesslerisation (Folin and Denis, A., 1916, ii, 573). Slight modifications of this method are described for the analysis of human milk. Urea in milk may be determined by the urease method (Marshall, A., 1913, ii, 640). Ten c.c. of human or 5 c.c. of cow's milk are treated with 2 c.c. of an extract of Jack bean for thirty minutes. The ammonia produced is carried over into standard acid by a stream of air and estimated by Nesslerisation.

In the estimation of creatine and creatinine, protein may be removed by metaphosphoric acid. The presence of lactose, however, intensifies the colour reaction with picric acid, and if this method is used, equivalent amounts of the sugar should be added to the standard solution. It is perhaps better to remove protein, fat, and lactose by copper sulphate and calcium hydroxide, and to apply the colour reaction to the clear, sugar-free filtrate. Amino-nitrogen is determined by the nitrous acid decomposition method of Van Slyke (A., 1912, ii, 1008). Protein must first be removed by precipitation with acetic acid and copper acetate. For the determination of uric acid, advantage is taken of the method described by Morris (A., 1916, ii, 456). The milk is treated with acetic acid and zinc acetate solution, and heated on the water-bath for fifteen to twenty minutes. After cooling and making up to a known volume, it is filtered, and an aliquot part of the filtrate treated with zinc acetate and sodium carbonate solution. The resulting precipitate is separated by centrifugalisation, washed, treated with acetic acid, and the zinc removed by hydrogen sulphide. Uric acid in the concentrated filtrate is estimated by the colour reaction with Folin and Denis's reagent (A., 1912, ii, 1011). Estimations of these non-protein nitrogenous constituents in cow's milk and human milk are given.

J. C. D.

A Multiple Pipette Holder for the Distribution of Serum for the Complement-fixation Test. Francois. H. Reynolds (*J. Agric. Res.*, 1918, **15**, 615—618).—The pipette holder consists of a brass tube 35 cm. long and 0·94 cm. external diameter, the two ends being closed by screws or caps, and having twelve side-tubes set in one plane perpendicular to it at equal intervals along it. Another tube, to serve as a mouthpiece, is fixed on the opposite side to these tubes. The twelve side-tubes, each being 0·6 cm. in internal diameter, are lined with rubber tubing, of which the free end is folded back over the mouth of each tube, and into these are inserted the graduated pipettes. In this way, twelve lots of serum may be withdrawn at once.

W. G.

General and Physical Chemistry.

Ultra-violet Band of Ammonia and its Occurrence in the Solar Spectrum. A. Fowler and C. C. L. Gregory (*Phil. Trans.*, 1919, [*A*], **218**, 351—372. Compare A., 1918, ii, 282).—The ammonia spectrum has been photographed (i) by means of a quartz spectrograph giving a dispersion of 60 Å. per mm. at λ 3360, (ii) by a quartz Littrow instrument having a dispersion of 7 Å. per mm., and (iii) by means of a 10 ft. grating giving a dispersion of 1·85 Å. per mm. In the first two cases an ammonia flame was used, obtained by feeding a blowpipe with ammonia and oxygen, whilst in the last case a copper arc burning in ammonia furnished the light. Long tables of wave-lengths are given, which are probably accurate to 0·01 Å.; these are compared with the Rowland values for the solar spectrum. From the comparison, it is evident that the band λ=3360 in the solar spectrum is due to ammonia, and also that many of the unidentified weaker lines of the solar spectrum are also due to ammonia. Photographs of the highly resolved band λ 3360 are appended to the paper. J. F. S.

Wave-length Measurement in Spectra from 5600 Å. to 9600 Å. W. F. Meggers (*Bull. Bureau of Standards* [*U.S.A.*], 1918, **14**, [3], 371—395).—The first-order spectra of lithium, sodium, potassium, rubidium, cæsium, copper, glucinum, calcium, strontium, barium, and magnesium have been photographed over the long wave regions 5600 Å. to 9600 Å. For this purpose, a concave grating of radius of curvature 640 cm. with a ruled surface 7·5 cm. by 13·3 cm. with 299 lines per mm. was employed, and was mounted in parallel light, the intensity of the spectra, compared with that afforded by the Rowland method of mounting, being quadrupled by this method of mounting. The device also secures freedom from astigmatism. Ordinary photographic plates are sensitised to the long wave region by being soaked for three to five minutes in a bath made by adding 4 c.c. of a solution of 1 part of dicyanin in 1000 parts of alcohol to 50 c.c. of distilled water, 50 c.c. of ethyl alcohol, and 5 c.c. of strong ammonia. The exposures were limited to thirty minutes. Arcs of metallic electrodes were employed wherever possible, Acheson graphite electrodes impregnated with large quantities of the respective salts being employed in other cases. A current of 6 amperes was employed for the region 6000 Å. to 7000 Å., 7 amperes for the region 7000 Å. to 8000 Å., and so on, except in the case of magnesium, a current of 3 amperes at 110 volts being employed in this case. The comparison spectra were afforded by that of an arc between Norwegian iron poles operated under standard conditions. The results obtained are expressed in tabular form, which afford ready comparison with the results of other observers. The intensities and other physical characteristics of the various lines are recorded. Illustrations of the spectra are

given in some cases. The probable error is less than 0·02 Å. for all lines measured more than twice. The frequency differences of doublets in the spectra of sodium, potassium, rubidium, cæsium, and copper are shown to be constant in most cases to 1 part in 100,000 in the number of waves per cm. J. S. G. T.

The Serial Constitution of Absorption Spectra. FRED. VLÈS (*Compt. rend.*, 1919, **168**, 1044—1047).—A continuation of previous work (compare A., 1914, ii, 400) in which the author, from a study of the absorption spectra of several substances, confirms his views as to the serial constitution of these spectra. W. G.

Absorption and Constitution of the Coloured Alkali Salts of Nitrotriphenylmethanes and Related Compounds. A. HANTZSCH and F. HEIN (*Ber.*, 1919, **52**, [*B*], 493—509. Compare A., 1907, i, 500; and Hedley, 1908, i, 382).—A comparison of the alkali salts of nitrotriphenylmethanes and nitrodiphenylamines, nitrohydrazobenzenes, and nitrodiazoaminobenzenes.

Triphenylmethane only forms a mono- and a tri-nitro-derivative. Diphenyl-*p*-tolylmethane (from benzhydrol and toluene by means of stannic chloride) reacts with fuming nitric acid to give 4 : 4′-*dinitrodiphenyl*-o-*nitro*-p-*tolylmethane*, m. p. 131°. *p*-Bromotriphenylmethane, however, gives 4-*bromo*-4′ : 4″-*dinitrotriphenylmethane*, white leaflets, m. p. 165·5°. The salts of nitrotriphenylmethanes are much less stable than those of the simple nitromethanes, and can scarcely be isolated. Solutions of the mononitro-compounds in alcohol remain colourless for a moment on the addition of sodium ethoxide, but reach the maximum yellow colour in about fifteen minutes. The absorption bands are similar to those of the mononitromethane *aci*-salts, but include a quinonoid band, showing that the salts have the simple quinonoid, as well as the *aci*-configuration, thus: $CHPh_2 \cdot C_6H_4 \cdot NO_2 + EtONa \longrightarrow CPh_2 : C_6H_4 : NO \cdot ONa$. The dinitro- and trinitro-compounds give violet salts, which have the "conjugated–quinonoid" configuration of the di- and tri-nitromethanes, thus:

$$C_6H_4Br \cdot C\langle \begin{matrix} C_6H_4 : NO_2 \\ C_6H_4 \cdot NO_2 \end{matrix} \rangle Na \quad \text{and} \quad NO_2 \cdot C_6H_4 \cdot C\langle \begin{matrix} C_6H_4 : NO_2 \\ C_6H_4 \cdot NO_2 \end{matrix} \rangle Na.$$

They also give violet salts with ammonia and aliphatic amines, but not with pyridine.

[With M. HARDTMANN].—*p*-Nitrodiphenylamine is best obtained by nitrating pure benzoyldiphenylamine and then hydrolysing by means of alcoholic potassium hydroxide. Its solution in alcohol is pale yellow, but becomes deep red on the addition of potassium hydroxide, owing to the formation of a para-quinonoid salt of the formula $NPh : C_6H_4 : NO_2K$. The *o*-nitrodiphenylamine is yellowish-red in alcoholic solutions, but the addition of potassium hydroxide has no effect. *p* : *p*′-Dinitrodiphenylamine, like the di-, tri-, and hexa-nitrotriphenylmethanes, gives deep violet salts. Strange to say, the salts of hexanitrodiphenylamine are only yellowish-red.

p-Nitrodiazoaminobenzene, *pp'*-dinitrohydrazobenzene, and *pp'*-dinitrodiazoaminobenzene also give violet salts. The last compound is obtained by the action of amyl nitrite on *p*-nitroaniline, but a drop of acetic acid is essential to the initiation of the reaction. Its *sodium* salt, $C_{12}H_8O_4N_5Na$, separates on cooling a solution in aqueous-alcoholic sodium hydroxide, in leaflets with metallic lustre and red streak, which are hydrolysed by cold water to the free aci-*dinitrodiazoaminobenzene*, $NO_2 \cdot C_6H_4 \cdot N{:}N \cdot N{:}C_6H_4{:}NO \cdot OH$. This looks so much like the salt that it has previously been unrecognised. It is even formed when dilute solutions of the ordinary dinitro-compound are boiled and quickly cooled, but it is immediately isomerised by alcohol. When slowly heated, it changes into the more stable form and then explodes at about 233°.

Absorption curves are reproduced in the original and discussed at some length partly in a controversial manner. J. C. W.

Absorption and constitution of the Simplest Triphenylmethane- and Azo-Dyes and Related Compounds. A. Hantzsch (*Ber.*, 1919, **52**, [*B*], 509—530).—The absorption bands of the simplest and most important dyes, namely, those of the triphenylmethane series and the azo-dyes, are compared with those of closely-related coloured substances, including the salts of the polynitrotriphenylmethanes (preceding abstract). It is shown that the original quinonoid formulæ given by E. and O. Fischer need only to be extended to conjugated-quinonoid structures to explain the optical properties, new schemes like those of Baker (T., 1907, **91**, 1490) being unnecessary.

In the case of the quinonoid salts of aminotriphenylmethanes, as in the case of the quinonoid alkali salts of nitrotriphenylmethanes, the maximum optical effect, that is, the typical colour, is already reached when there are two salt-forming groups in the molecule. A third amino-group actually has, if anything, a hypsochromic effect. A hydroxyl or methoxyl group in the place of a third amino-group has about half the optical effect; for example, hydroxy- and methoxy-malachite-greens are midway between malachite-green and crystal violet. Tetramethyldiaminorosaniline gives solutions of many colours, from bluish-red to yellow, in indifferent media, but they all give absorption curves like that of magenta, only more or less displaced.

The magenta dyes also closely resemble the reddish-violet salts of the aminoazobenzenes, and the three classes are, therefore, characterised by two components: (1) a quinonoid salt complex (*aci*nitro-salt or ammonium salt) as chromophore, and (2) another group (nitro- or amino-) which forms a powerful auxochrome in conjugation with the quinonoid group, thus:

$ArC{=}C_6H_4{=}NO_2$	$ArC{=}C_6H_4{=}{=}NR_2$	$N{=}C_6H_4{=}{=}NR_2$
$Ar{\cdot}NO_2 \ldots . M$	$Ar{\cdot}NR_2 \ldots X$	$NAr{\cdot}R \ldots . X$
Nitrotriphenylmethanes.	Aminotriphenylmethanes.	Aminoazo-salts.

The effect of an acid on compounds of the last types is obviously to break the conjugation and so destroy the auxochrome.

Two new compounds are described. *Dimethoxydimethylaminotriphenylcarbinol*, $(OMe\cdot C_6H_4)_2C(OH)\cdot C_6H_4\cdot NMe_2$, bundles of very pale green crystals, m. p. 112°, is obtained by heating together dianisyl ketone, dimethylaniline, and a mixture of phosphorus penta- and oxy-chlorides, and is converted into *dimethoxyfuchsondimethylimonium chloride*, $(OMe\cdot C_6H_4)_2C{:}C_6H_4{:}NMe_2Cl$, by means of hydrochloric acid. This dye has the typical appearance of cantharides, but it is not fast to light or washing.

Several sets of curves are reproduced in the original, but the lengthy discussion is largely polemical. J. C. W.

Relationship between Mechanical and Chemical Rotation and the Structure of Liquid Crystals. O. Lehmann (*Ann. Physik*, 1919, [iv], **58**, 631—656).—A continuation of previously published work (*ibid.*, 1916, **51**, 353). The effects produced when the containing walls which hold liquid crystals are twisted whilst polarised light is passing through the crystals are investigated. The effects are examined by means of crossed nicols for *p*-azoxyphenetole and for the same substance to which colophony and cholesteryl benzoate have been added. Numerous diagrams of the appearance under the nicols are given. J. F. S.

The Rotation Dispersion of Butyl, Heptyl, and Octyl Tartrates. Percy Faraday Frankland and Frederic Horace Garner (T., 1919, **115**, 636—661).

Evolution of Very Dilute Solutions of Tetrachloroplatinic Acid in Complete Darkness and at Different Temperatures. Marcel Boll (*Compt. rend.*, 1919, **168**, 1108—1111).—A comparison of the changes and their velocities taking place in a very dilute solution of tetrachloroplatinic acid in the dark at temperatures between 10° and 100°, and those taking place in the light (compare A., 1912, ii, 407). The thermal acceleration is practically the same whether the action takes place in the dark or under the influence of high-frequency rays. W. G.

Collision of α-Particles with Light Atoms. I. Hydrogen. Sir E. Rutherford (*Phil. Mag.*, 1919, [vi], **37**, 537—561. Compare E. Marsden, A., 1914, ii, 407; Marsden and Lantsberry, *Phil. Mag.*, 1915, [vi], **30**, 240).—"H"-particles, derived by passing α-particles through hydrogen, from "head-on" collisions between the α-particles and the nuclei of the hydrogen atoms, are also obtained, without using hydrogen, from thin-walled glass and quartz tubes filled with radium emanation, and from a deposit of radium-*C* on a nickel plate—from the latter more than the former. Special experiments showed that radium-*C* is not different in this respect from radium-*A* and the emanation, and these have also shown that oxygen and nitrogen atoms (see succeeding papers) can be put in

swift motion by collision with α-particles to cause scintillations outside the range of the α-particles, to which, probably, a large number of the scintillations, ascribed by Marsden to H-particles, were due. The homogeneous α-rays of radium-*C* deposited on a metal disk were exclusively used. The disk was washed with alcohol and heated in an exhausted tube to 300° for a minute to reduce "volatilisation" of the radium-*C* (Ratner). The H-particles were counted by the scintillations on zinc sulphide screens, and were similar to those produced by α-particles 3 mm. from the end of their range. The active disk was mounted in a tube capable of exhaustion, or of being filled with the gas studied, at a variable distance from an opening in the end covered with thin sheets of silver, aluminium, or iron of stopping power equivalent to from 4 to 6 cm. of air, the zinc sulphide screen being just outside the apparatus. The number of H-particles is ordinarily less than one in one hundred thousand of the α-particles, and can only be detected after the latter have been absorbed. β-Rays were suppressed by a strong magnetic field. The number of H-particles without any gas in the vessel was first determined. These are small in number relatively to those produced when the apparatus is filled with hydrogen, and it cannot be decided whether they originate from the radio-element itself or from hydrogen occluded by the materials in which it is contained. The number fell off, when metal screens were interposed, rapidly between the equivalent of 7 and 12 cm. of air, and then more slowly, a few being observed up to the equivalent of 28 cm. The metal screens—silver and aluminium—were heated to drive off occluded gases. Gold was found to be very free from hydrogen, but could not be used close to the zinc sulphide screen on account of the marked luminosity it produces on the screen beyond the range of α-particles, an effect that is being investigated.

The number of H-particles produced in hydrogen gas and their distribution with velocity differed markedly from the results calculated from the simple theory by Darwin's formula. The apparatus being filled with hydrogen at atmospheric pressure, the number of H-atoms was counted when aluminium foils were interposed before the screen. There was no diminution between the equivalent of 9 and 19 cm. air absorption, and then a slow decrease in the number took place, followed by a rapid one near the end of the range. Theoretically, between 9 and 19 cm. the number should have been reduced to 28%. This is only marked when long-range α-particles are used. As the range of the α-particles is reduced, the theoretical curves are more and more nearly approached. The absorption curve for H-particles produced by long-range α-particles is similar to that of the α-particles themselves, showing that the hydrogen atoms are thrown forward all at practically the same velocity and in the same direction as the α-particle is travelling, or at least within 10° or 15° from it. The fraction of the number of α-particles which produce one H-particle per cm. of path in hydrogen at *N.T.P.* was found to be about 10^{-5}. At 10 cm.

(eq. air absorption), the total number produced is ten times, at 19 cm. thirty-one times, the number calculated from the simple theory (Darwin). On the average, each α-particle of 7 cm. range of radium-*C* produces an H-particle when the perpendicular distance of its path from the centre of the hydrogen atom is equal to or less than $2{\cdot}4 \times 10^{-13}$ cm., and the results point to the view that within $3{\cdot}5 \times 10^{-13}$ cm., the field of force between the colliding nuclei undergoes rapid changes in magnitude, and probably direction. Since only one in 10^5 α-particles passing through 1 cm. of hydrogen produces an H-particle, and in this distance each α-particle passes through 10^4 hydrogen molecules, only one out of every 10^9 collisions produces an H-particle capable of being detected beyond the range of the α-rays. The helium nucleus, or α-particle, is pictured as a charged disk of radius about $3{\cdot}6 \times 10^{-13}$ cm., with its plane perpendicular to its direction of motion, and probably composed of four hydrogen nuclei and two nuclear electrons. This is regarded as being probably much deformed during close collisions. It is to be expected that it would break up, but no evidence of this has yet been observed. F. S.

Collision of α-Particles with Light Atoms. II. Velocity of the Hydrogen Atom. Sir E. Rutherford (*Phil. Mag.*, 1919, [vi], **37**, 562—571).—The assumption in the preceding paper that the long-range scintillations observed in hydrogen are due to hydrogen atoms set in swift motion by their collision with α-particles is supported by their range, which agrees with that calculated for such H-particles by Darwin from Bohr's theory. The mass, charge, and velocity of these H-particles have been determined by measurements of the deflection they undergo in electromagnetic and electrostatic fields. As source of hydrogen, a film of paraffin wax 30 μ in thickness exposed to intense α-rays was used. The H-particles were passed through two slits and received on an external zinc sulphide screen, after passing through a sheet of iron, closing the end of the apparatus, equivalent in stopping power to 4 cm. of air. With the apparatus exhausted, the deviation in a magnetic field of the α-particles themselves was first found. The paraffin film and aluminium screens, equal in total stopping power, with the iron sheet, to 14·4 cm. of air, were then interposed, and the deflection of the H-particles found to be 1·45 times that of the α-particles of radium-*C*. This gives for mu_0/e, the product of the mass and initial velocity of the fastest H-particles divided by the charge, $3{\cdot}15 \times 10^5$. From theory, u_0 should be 1·6 v_0, that is, 1·6 times that of the α-particles, and mu_0/e $3{\cdot}2 \times 10^5$. All the H-particles carried a positive charge, and no sign of negatively charged particles was observed. The electrostatic deviation between two parallel plates 6 cm. long and 1·55 mm. apart charged to 4500 volts was insufficient to deviate the H-particles completely, and it was calculated that 30,000 volts would be required. So the deflexion with a magnetic field was compared with that produced by a combined electrostatic and electromagnetic field acting in unison, and it was

found that a magnetic field of 238 gauss on the average was equivalent to an electric field of 1000 volts. This gives for u_0 the maximum velocity of the H-particle, $3{\cdot}12 \times 10^9$ cm. per second. The calculated value, $1{\cdot}6\ v_0$, is $3{\cdot}07 \times 10^9$ cm. per second. The value of e/m, consequently, is 10^4 e. m. units, which agrees very well with the value, 9570, for the H-ion in the electrolysis of water. This proves that for close collisions the conservation of momentum and energy holds good, and that there is no sensible loss of energy due to radiation.

The energy communicated to the H-particle is 0·64 that of the α-particle, and, after traversing the equivalent of 12 cm. of air, is 0·44, corresponding with that of an α-particle of range 2 cm. of air. The brightness of the scintillation it produces is, at all ranges, much less than is to be expected, and corresponds, for example, with that of an α-particle of range 0·5 cm. instead of 2 cm. This may be due to the energy spent per unit of path by an H-particle being only about one-sixth of that by an α-particle. A large proportion of instantaneous double scintillations was observed, and it was found, in comparison with α-particles, that the number was nearly double what is to be expected from probability considerations. It could not be settled, however, whether this effect is real or due to the eye being unable to distinguish separately the weak scintillations due to H-particles as readily as those produced by α-particles. F. S.

Collisions of α-Particles with Light Atoms. III. Nitrogen and Oxygen Atoms. Sir E. Rutherford (*Phil. Mag.*, 1919, [vi], **37**, 571—580).—From Bohr's general theory of the absorption of charged atoms in passage through matter, which is substantiated experimentally for the α-particles and H-particles, the range x in hydrogen of an atom of charge e and mass m moving with a speed equal to that of an α-particle of range R is given by $x/R = mE^2/Me^2$, M and E being the mass and charge of the α-particle. For light atoms, with unit charge $x = mR$. Tables are given for x/R for singly charged atoms from hydrogen to gold travelling with a velocity calculated to be produced by impact of the atom in a "head-on" collision with the α-particle. For α-particles of range 7 cm., the maximum ranges in cm. to be expected are as follow: He 28, Li 19·6, Gl 15·4, B 12·4, C 11·2, N 9·3, O 7·8. Experiments with helium have shown that, if any long-range particles are produced, the number is very small compared with that produced in hydrogen, and it is concluded that the helium atoms carry a double charge and have the same range as the α-particles. Neither were any certain indications of long-range particles obtained for salts of lithium, glucinum, and boron. Such experiments are much easier for gases, and in air numerous bright scintillations are observed for distances 2 cm. beyond the range of the α-particles. With a total absorption equivalent to 7·5 cm. of air, these "N-particles" and "O-particles" give scintillations equal in brightness to an α-particle of range about 1 cm. The scintilla-

tions for oxygen and carbon dioxide were of about the same range and brightness as those in air, but they were shown to arise in the gases, and not to be emitted from the radio-element itself. No evidence of singly charged carbon atoms from carbon dioxide was obtained. Estimating the relative numbers of high-speed particles in hydrogen, oxygen, and nitrogen, it was found that the numbers for the different gases are not very different. The long-range rays of range 11·3 cm. found by Rutherford and Wood in the active deposit of thorium (A., 1916, ii, 282) are such as would result from oxygen atoms present in the mica screens used, but the number—1 to 10,000 α-particles—was much greater than is to be expected from the experiments with radium-*C*, and further experiments are in progress. F. S.

Collisions of α-Particles with Light Atoms. IV. An Anomalous Effect in Nitrogen. Sir E. RUTHERFORD (*Phil. Mag.*, 1919, [vi], **37**, 581—587).—A surprising effect was noticed in the study of the "natural" scintillations due to H-particles, which it is difficult to decide whether they are due to the action of α-particles on occluded hydrogen in the radioactive material or support, or are expelled in the disintegration itself. With the apparatus described in the first paper, exhausted and filled with dry oxygen or carbon dioxide respectively, the number of natural scintillations observed diminished in about the ratio to be expected from the stopping power of the gas column. In dried air, however, the number increased, and with a total absorption equivalent to about 19 cm. of air was twice as great as with the apparatus exhausted. All experiments were made at absorptions greater than the equivalent of 9 cm. of air to eliminate the O-particles and N-particles described in the last paper. The additional H-particles were not due to moisture or dust nuclei, and were observed in chemically prepared nitrogen, from ammonium nitrate, to an extent 1·25 times that observed for air. They were shown to arise from the volume of the gas, and were not due to a surface effect in the radioactive source. The H-particles so obtained from nitrogen had a somewhat greater penetrating power than those from hydrogen, but none could be detected beyond a range of 28 cm., and probably the difference is due to their being projected more in the line of flight of the α-particles than those resulting from hydrogen gas. The number from nitrogen at atmospheric pressure is equal to the number given in hydrogen at 6 cm. pressure, so that only one H-particle is given in nitrogen for every twelve collisions giving rise to N-particles. As regards both the brightness of the scintillations and the range, these long-range particles closely resemble, and in all probability are, H-particles, but to settle the point definitely it will be necessary to determine their deflexion in a magnetic field. Preliminary experiments indicate a similar deflexion, but to decide the question definitely it will probably be

necessary to employ a solid nitrogen compound free from hydrogen, and to discriminate between H-particles and possible particles of atomic mass 2.

If they are H-particles, it must be concluded that the nitrogen atom has been disintegrated during the close collision with an α-particle, and that the hydrogen nucleus is a constituent part of the nitrogen nucleus. This may account for the ranges of the N-particle and O-particle being the same, instead of differing by some 19%, as is to be expected. For if hydrogen is disrupted from the nitrogen atom, the energy of the impact would be shared between the two systems. Nitrogen is the only light atom of atomic mass $4n+2$, where n is a whole number, and its nucleus should consist of three helium nuclei and ten hydrogen nuclei. The latter may be outsiders of the main system of mass 12, and the close collision with an α-particle seems to be the most likely agency to promote the disruption of such a nucleus. It is not to be expected, a priori, that the velocity or range of H-particles, so produced from the nitrogen atom, should be identical with that of those produced by collisions in free hydrogen. F. S.

Precision-measurements in the *X*-ray Spectra. Manne Siegbahn (*Phil. Mag.*, 1919, [vi], **37**, 601—612).—By a new method of measurement, the accuracy of wave-length measurements for *X*-rays has been increased a hundred-fold. The angle of the reflected rays is determined as the angle through which the same photographic plate has to be turned in order to receive impressions of the nth order reflection on both sides of the direct ray, the angles being read off an accurate circle scale. If ϕ is the angle of reflexion, and the plate is turned accurately 4ϕ (and the crystal nearly $2\phi+180°$), the spectral lines on both sides would cover one another. In practice, the plate is turned nearly 4ϕ, and by measuring the distance between the lines, the small correction to exactly 4ϕ can readily be applied.

The plate and slit must have the same distance from the rotating axis of the reflecting face of the crystal and of the plate-holder, and during exposure the crystal may, if necessary, be continually turned through a small range, and for bad crystals irregularities so eliminated. Drawings of a spectrograph for vacuum built on this principle are given, and also for the *X*-ray tube found most suitable.

The wave-length of Cu$K\alpha$ (the α-line of the *K*-series of copper) was determined to be $1537{\cdot}358(\pm 0{\cdot}033)\times 10^{-11}$ cm., when the lattice constant, d, of rock-salt is taken as $2{\cdot}81400\times 10^{-8}$ cm., and of calcite $3{\cdot}02904\times 10^{-8}$ cm. The relation of these two constants was accurately determined for Cu$K\alpha$, Fe$K\alpha$, and Sn$L\alpha$, the wave-lengths found for the last two lines being 1932·39 and 3592·94 respectively. The lattice constant found for potassium ferrocyanide was $8{\cdot}408\times 10^{-8}$, instead of the value 8·454 used by Moseley, and

the latter's wave-length tables must be diminished by 0·54% in consequence. The following table of wave-lengths is given:

Element.	Atomic number.	$\lambda \cdot 10^{-11}$ cm. $K\alpha_1$.	$K\beta_1$.
Chlorine	17	4718·70	—
Potassium	19	3733·86	3447·37
Calcium	20	3351·86	3087·89
Scandium	21	3025·26	2774·54
Chromium	24	2285·17	2081·44
Iron	26	1932·39	1753·97
Cobalt	27	1785·24	1617·58
Nickel	28	1654·67	—
Copper	29	1537·36	1389·53

This great increase of experimental accuracy is employed to test the formulæ of Sommerfeld for the difference of wave-length between the α_1 and α_2 doublet of copper in the K-series with the result, $0{\cdot}373(\pm 0{\cdot}005) \times 10^{-8}$, in complete agreement with theory. Preliminary measurements of the wave-length difference of the β- and β'-lines of iron, manganese, and chromium give 3·55, 4·55, and 4·87($\times 10^{-11}$ cm.) respectively. The formulæ of the $K\alpha$-series given by Moseley, Sommerfeld, Debye, and J. Kroo are compared with the experimental values given in the above table, with results decidedly in favour of the formula of the last-named, the difference between the calculated and experimental results varying regularly from $-0{\cdot}2\%$ for chlorine to $+0{\cdot}017\%$ for copper. F. S.

Ionisation by Canal Rays. J. Stark (*Jahrb. Radioaktiv. Elektronik*, 1918, **15**, 329—364).—A summary of the literature of the subject with a bibliography. The account is divided into three chapters: (1) emission of electrons from metallic surfaces; (2) emission of electrons from gases; (3) emission of positive ions by canal rays. E. H. R.

The Theory of Electrolytic Ions. X. The Conductivity of Multi-valent and Multi-stage Electrolytes. Richard Lorenz (*Zeitsch. anorg. Chem.*, 1919, **106**, 49—75).—A theoretical paper in which the general theory of electrical conductivity is discussed from the viewpoint of Planck's conductivity equation. It is pointed out that the conventional use of normal solutions and equivalent conductivities leads to much confusion. It is better to refer all measurements to molecular quantities, no assumption being then made as to the manner in which the electrolyte dissociates. The degree of dissociation is independent of the manner in which it takes place, and is simply defined as the ratio of the number of altered molecules to the number originally present. The molecular conductivity quotient μ/μ_∞ has been deduced from Planck's equation for a number of different, typical kinds of ionic dissociation. This quotient is identical with the degree of dissociation only in the case of single-stage electrolytes, that is, of those which dissociate in one stage, whatever be the number of different

ions formed. In the case of multi-stage dissociation, the conductivity quotient bears no relation to the degree of dissociation and is generally smaller than this. E. H. R.

Cause of the Small Electrical Conductivity of Non-aqueous Salt Solutions. R. Beutner (*Zeitsch. Elektrochem.*, 1919, **25**, 97—100).—From a series of electrical conductivity measurements of solutions of salicylic acid and dimethyltoluidine in nitrobenzene solution, the author asserts that the cause of the slight conductivity of solutions of salts in non-aqueous solutions is a non-electrolytic dissociation which opposes the electrolytic dissociation. This is supported by the observations that a solution of an acid or a base in a non-aqueous solvent has a very slight conductivity, whilst a similar solution of acid and base has a very much larger conductivity. The conductivity of a solution of acid and base changes regularly when the concentration of the acid is changed, the base being kept constant and vice versâ. Further, the molecular conductivity decreases with increasing dilution. It is stated that the above observations are in keeping with the assumption that in most non-aqueous solvents an equilibrium salt $\rightleftharpoons$ acid + base exists, so that both free acid and base exist side by side with the salt. Hence the salt, as such, has a considerable conductivity, whilst the acid and base alone have practically none. J. F. S.

Contra-electromotive Force of Polarisation in Sulphuric Acid. Albert Noyes (*Compt. rend.*, 1919, **168**, 1049—1052).—The contra-electromotive force of sulphuric acid at 20° is 1·68 volts, and diminishes at first inversely as the absolute temperature. Between 60° and 120°, it diminishes more rapidly, and above the latter temperature remains practically constant. This may be attributed to a difference in the mode of ionisation, which is at first into H^+ HSO_4^- and then $2H^+$ and SO_4^-. W. G.

The Potential of a Nitrogen Electrode. Francis Lawry Usher and Ramavenkabasubbier Venkateswaran (T., 1919, **115**, 613—618).

The Chemical Process of the Lead Accumulator. Ch. Féry (*Bull. Soc. chim.*, 1919, [iv], **25**, 223—234).—The author considers that the theory of "double sulphating" is incorrect, and that the behaviour of the lead accumulator is similar to that of a primary cell with a solid depolariser, with the difference that the negative electrode gives rise to an insoluble salt. The reaction during normal discharging and charging is given by the reversible reaction:

$$2Pb + H_2SO_4 + Pb_2O_5 \rightleftharpoons Pb_2SO_4 + H_2O + 2PbO_2.$$

The subsulphate is a black powder and, unlike the normal sulphate, has a certain conductivity. The higher oxide, the active material of the positive electrode, is a black, endothermic substance and a powerful oxidising agent. W. G.

Relationship between Electrolysis and Photolysis and Electrolytic Non-reversibility. Emil Baur (*Zeitsch. Elektrochem.*, 1919, **25**, 102—109).—The author regards photolysis as analogous to a type of electrolysis. If a substance E absorbs a light quantum it becomes polarised and a potential difference is set up. This is symbolically expressed by the equation $E + h\nu = E\overset{\oplus}{\ominus}$ This conception of photolysis is compared with electrolytic action, and it is shown that the electrolysis of sodium acetate and the photolysis of acetic acid yield the same products and respectively are to be expressed by similar equations, thus: $2CH_3\cdot COO' + 2F = C_2H_6 + 2CO_2$; $U^{VI}\begin{cases}\oplus\oplus + 2CH_3\cdot COO' \\ \ominus\ominus + U^{VI}\end{cases} = C_2H_6 + U^{IV} + 2CO_2$. Glycollic acid in the presence of oxidising agents, such as ferric salts, cupric salts, or uranyl salts is converted into formaldehyde under the influence of light, and it is experimentally shown that electrolysis gives the same product. Oxalic acid is converted by light in the presence of uranyl salts into carbon monoxide and carbon dioxide, but it was found impossible to detect carbon monoxide in the products of electrolysis of oxalic acid. In the light of the present theory the author re-states with modifications the theory recently (A., 1913, i, 443) advanced with regard to the initial stages of the assimilation of carbon dioxide by plants. J. F. S.

Disgregation of the Oxidation Products Produced on Silver Anodes in Alkaline Media. Fr. Jirsa (*Zeitsch. Elektrochem.*, 1919, **25**, 146—151).—A silver anode which has been polarised in alkaline solution by direct current is temporarily depolarised by telluric acid, whilst alternating current with simultaneous polarisation by direct current makes an over-voltage on the anode impossible and depolarises permanently. When a silver anode in an alkali hydroxide is polarised by alternating current alone, it is oxidised, the current being effective only as far as its anodic component is concerned. The oxidation product, produced when an alkali hydroxide is electrolysed between silver electrodes, disperses itself throughout the solution as a colloidal suspension. When direct current is employed the suspension is Ag_2O_2, but if the solution of alkali contains telluric acid the suspension produced consists of Ag_2O_3; with alternating current the oxide Ag_2O is produced. J. F. S.

Size of Particle, Solution Tension, and Sintering. E. Podszus (*Zeitsch. Elektrochem.*, 1919, **25**, 100—101).—A theoretical paper, in which a paper by Kohlschütter and Vuilleumier (this vol., ii, 9) is criticised. J. F. S.

An Explanation of Space-filling Numbers. Richard Lorenz (*Zeitsch. anorg. Chem.*, 1919, **106**, 46—48).—It has been shown (this vol., ii, 212) that, for a number of univalent inorganic cations, the space-filling number ψ increases regularly with the number of

atoms in the ion. The space-filling number is a ratio of two volumes, that is, of the absolute volume of the ion, ϕ, to the ionic volume V_0 calculated additively from the usual atomic volumes of the constituent atoms. Since then the ratio increases as the number of atoms increases, it follows that ϕ increases at a greater rate than V_0, that is to say, ϕ increases more rapidly than it would do if it were an additive quantity. This can only be explained on the assumption that, when the atoms combine, a certain amount of interstitial space is included in the molecule, with the result that the ratio of the absolute volume of the molecule to the volume of its "sphere of influence" gradually increases as the molecule becomes more complex. E. H. R.

Deduction of Cryoscopy from the General Laws of Solubility. Albert Colson (*Compt. rend.*, 1919, **168**, 1047—1049).—A mathematical discussion, in which the author, starting with his law of solubility, deduces Raoult's law. W. G.

High Temperature Researches. XII. The Measurement of Vapour Tensions at Very High Temperatures with some Observations on the Solubility of Carbon in Metals. Otto Ruff and Bernhard Bergdahl (*Zeitsch. anorg. Chem.*, 1919, **106**, 76—94).—A new method has been devised for measuring the vapour pressures of metals at high temperatures and for the determination of their boiling points. The method consists in observing the gradual loss of weight occurring whilst the metal is exposed to a gradual, uniform rise of temperature to beyond its boiling point. The loss of weight is plotted against the temperature, and from the curve so obtained the boiling point is estimated. Before the boiling point is reached the curve is approximately logarithmic, and beyond this point becomes linear, but the change at the boiling point is not as sharp as might be expected. For the determinations, a small quantity of the metal, about 0·5 gram, is heated in a very small crucible of quartz or carbon. The crucible is suspended from a specially designed spring balance, by which the loss of weight is observed, and hangs inside a resistance furnace which can be evacuated and filled with an indifferent gas at any desired pressure, which is recorded by a manometer. Special provision is made to ensure a uniform rate of rise of temperature. The following results are recorded for the boiling points: mercury, 357°; cadmium, 785°; zinc, 930°; arsenic, 568°; antimony, 1330°; bismuth, 1490°; lead, 1555°; tin, 2270°; copper, 2305°; silver, 1950°; gold, 2600°. The results are compared with those of other observers, and in the cases of mercury, zinc, and cadmium, for which metals the older measurements are considered to be fairly trustworthy, the agreement is very satisfactory. The results for the vapour pressure of mercury agree well with those of Ramsay and Young (T., 1886, **49**, 453) at temperatures near the boiling point, but at lower temperatures the divergence is considerable. The new method appears to be more accurate near the boiling point.

When the measurements were made in carbon crucibles, the metal became saturated with carbon, and it was possible to estimate the solubility of carbon in the metals antimony, bismuth, lead, tin, copper, silver, and gold. In all cases the solubility was found to be too low to influence the boiling-point determinations. The solubility is highest in lead (0·094% at 1555°) and antimony (0·094% at 1327°), and in the other metals little more than a trace of carbon is dissolved. E. H. R.

Vapour Tensions of the Metals. J. W. Richards (*J. Franklin Inst.*, 1919, **187**, 581—598).—A theoretical discussion on the vapour pressures of liquid and solid metals in connexion with Trouton's rule and Richards' rule. The many equations for expressing vapour pressure as a function of the temperature are discussed. Tables are given of vapour pressures and the latent heats of vaporisation of some forty-three elements, in the former case for the solid at 0° and at the melting point; and the equations for calculating the vapour pressure at any temperature are given for both the solid and liquid. The practical significance of the vapour pressure is indicated in (1) the distillation of metals (Parkes', desilverisation process), (ii) loss of zinc in brass melting, (iii) loss of metal as fumes, (iv) sherardising and calorising, and (v) vapour losses during electrolysis. J. F. S.

A New Laboratory Fractionating Column and the Measure of its Efficiency. M. H. Robert (*Compt. rend.*, 1919, **168**, 998—1001).—The column is really a double one. The lower column is an ordinary bulb fractionating column with beads, but it is surrounded by a glass vacuum jacket, which is highly evacuated. Above this column and sealed on to it is another simple fractionating column, surrounded by an outer jacket through which air is caused to circulate, and on top of this is the still-head. The column gave very satisfactory results with mixtures of alcohol and water, acetic anhydride and acetic acid, benzene and toluene, in the extraction of hexahydrotoluene from essence of Borneo, and in the fractionation of light petroleum. Using the formula $E=(a-b)/v$, and applying it to the benzene–toluene mixture, where v is the amount of benzene in the original mixture and a and b are the amounts of benzene and toluene in the first half of the distillate, the efficiency of the column was found to be 0·94 as against 0·73 for a Vigreux column and 1·0 for a perfect column. W. G.

Direct Determination of the Temperature Exponent in the Equation of State of Fluids. E. Ariès (*Compt. rend.*, 1919, **168**, 930—933).—Knowing the values of T_c, P_c, and of the vapour pressures as well as the volumes v_1 and v_2 at a given temperature, the author has determined the value of n in the equation $(v_1-v_2)=RT_cx(\gamma_1-\gamma_2)/8P_c\tau^{n+1}$, for each of the seven substances for which the formula was obtained (compare this vol., ii, 184). The accuracy of these determinations has been tested by calculating the

variations of $(\nu_1 - \nu_2)$ with temperature and comparing the results against those observed by Young. The agreement is good. The values obtained for n increase by 0·04 for each increase of three atoms in the molecule of the substance, and there is an indication that the value of n for diatomic and triatomic substances must be close to but just greater than unity, that is, between 1 and 1·06.

W. G.

The Theory of the Gasification Process. [Producer Gas.] Wa. Ostwald (*Chem. Zeit.*, 1919, **43**, 229—231).—Three fundamental thermo-chemical equations represent the changes occurring in a gas producer: (1) $C + O_2 = CO_2 + 97{\cdot}6$; (2) $C + 2H_2O = CO_2 + 2H_2 - 18{\cdot}8$; (3) $C + CO_2 = 2CO - 38{\cdot}8$. If the carbon is utilised in these three changes in the relative proportions a, b, and c respectively, the complete process may be represented by the equation $(a+b+c)C + aO_2 + 2bH_2O = (a + b - c)CO_2 + 2bH_2 + 2cCO + 97{\cdot}6a - 18{\cdot}8b - 38{\cdot}8c$. Only two of the quantities a, b, and c are independent variables, and any desired values are readily represented by means of triangular co-ordinates after the manner introduced by Gibbs. Any point in the diagram may be represented by the equation as above. The values of a, b, and c can readily be determined from an analysis of the gas produced. The area of the triangle of reference is divided into two regions: (1) a region of combustion and gasification, and (2) a region of gas regeneration. Illustrations are given of the respective situations in these regions of the various technical gas mixtures. The author shows how isothermals or isocalorics are to be diagrammatically represented, and how an isocaloric solid may be constructed in any given case. The diagrams enable the thermo-chemical and volumetric characteristics of the process under any given circumstances to be readily ascertained, and to determine the effect of alteration of working on the course of the reactions, the coal consumed, the heating value of the gas obtained, etc.

J. S. G. T.

Critical Temperatures of Solution in Aniline of the Principal Hydrocarbons occurring in Light Petroleum. G. Chavanne and L. J. Simon (*Compt. rend.*, 1919, **168**, 1111—1114).—The temperature measured was in each case that above which the mixture of aniline and hydrocarbon was homogeneous, no matter what its composition. The hydrocarbons examined were those occurring in light petroleum, b. p. below 150°. The straight chain aliphatic hydrocarbons had practically the same critical temperature of solution, 71°, regardless of their molecular weight. Similarly, the β-methyl hydrocarbons all had a critical temperature of solution of about 74°. The cyclic hydrocarbons, *cyclo*hexane, etc., had critical temperatures very much lower than those of the corresponding straight chain hydrocarbons, and again the substitution of a methyl group had a marked effect. For isomeric hydrocarbons, the critical temperatures and the densities varied in an inverse ratio.

W. G.

Density and Temperature. W. Herz (*Zeitsch. Elektrochem.*, 1919, **25**, 145—146).—A theoretical paper in which the change of density in homologous series with temperature change is considered. It is shown that whilst the density of the members of homologous series at low and medium temperatures can show both a rising and a falling density with increasing number of carbon atoms, at high temperatures, near the critical point, the density increases regularly with increasing number of carbon atoms. The ratio of the densities of two members of an homologous series increases regularly with increasing temperature. J. F. S.

Regularities in the Magnitudes of Molecular Volumes. Fritz Ephraim and Eduard Michel (*Helv. Chim. Acta*, 1919, **2**, 266—276).—A further discussion on molecular volumes and the percentage contraction on the sum of the constituent atomic volumes (compare A., 1917, ii, 535). Tables are given showing the percentage contraction, calculated according to the equation $c = \text{mol. vol.} \times 100/\Sigma$ at. vol., for compounds of the alkali metals with most of the atoms or radicles, F, Cl, Br, I, O, OH, SO_4, SeO_4, NO_3, ClO_3, ClO_4, IO_3, IO_4, MnO_4, the necessary data and the authorities being quoted in another summary. Comparing the compounds with a fixed negative part, the percentage contractions are very similar, the cæsium haloids exhibiting the only abnormally great contractions. Comparing the various salts of one metal, however, great variations appear, fluorides showing contractions of about 62% and iodides about 30%. In spite of the uncertainty of much of the data, sufficient regularities are revealed to make it worth while to pursue such a line of inquiry further. J. C. W.

Standard Substances for the Calibration of Viscometers. E. C. Bingham and R. F. Jackson (*Bull. Bureau of Standards, U.S.A.*, 1918, **14**, [1], 59—86).—As liquids of greater viscosity than water, solutions of sucrose and mixtures of ethyl alcohol and water are suitable and convenient for use in calibrating viscometers. The viscosities of ethyl alcohol–water mixtures have been determined by several observers, with fairly concordant results, but the accuracy of existing data relating to sucrose solutions has been questioned. In the present work, the viscosities of 20% and 40% solutions of sucrose (by weight) were determined at temperatures from 0° to 100°, and that of a 60% solution from 10° to 95°, with results generally somewhat higher than those obtained hitherto. Existing data relating to the viscosity of water were also reviewed and corrected, the viscosity and fluidity being calculated for every degree from 0° to 100°. In discussing the relative merits of absolute and specific units for expressing viscosity, the centipoise (cp., the one-hundredth part of the *C.G.S.* unit) is favourably considered. By the use of this unit, the absolute and specific viscosities of a liquid are practically the same, provided that water at 20° be taken as the standard. The most probable value for the viscosity of water at 20° was found to be 1·005 cp.

W. E. F. P.

Occlusion of Hydrogen by the Metallic Elements and its Relation to Magnetic Properties. DONALD P. SMITH (*J. Physical Chem.*, 1919, **23**, 186—202).—A theoretical paper in which the literature on the occlusion of hydrogen by metals is discussed. It is shown that the alloys produced when hydrogen is occluded by metals are to be sharply distinguished from other types of binary hydrogen compounds (KH, SbH_3), and that these and the hydrogen-occluding metals occupy definite sharply divided regions of Werner's periodic table. The power of occluding hydrogen is compared with the magnetic properties of the metals, and it is shown that elements with a specific magnetic susceptibility greater than $0{\cdot}9 \times 10^{-6}$ at the ordinary temperature occlude hydrogen strongly, whilst those with a smaller susceptibility do not occlude hydrogen. Possible exceptions to this generalisation are copper, rhodium, and thorium. Hence it is concluded that the capacity of a metal to occlude hydrogen in large amounts is restricted to those of strongly magnetic character. A fairly comprehensive bibliography of the occlusion of hydrogen by metals is appended to the paper. J. F. S.

The Surface Condensation (Adsorption) of Water-vapour and Gases and the Errors in Weighing arising Therefrom. K. SCHERINGA (*Pharm. Weekblad*, 1919, **56**, 94—107).—A review of the literature bearing on this subject. The author concludes that errors in weighing due to the true adsorption of water vapour or air on the surface of the most commonly occurring substances may be neglected. W. S. M.

Adsorption of Electrolytes by Charcoal. PETER RONA and LEONOR MICHAELIS (*Biochem. Zeitsch.*, 1919, **94**, 240—260).—All salts, acids, and alkalis are adsorbed by charcoal, the anions and cations being adsorbed in equivalent amounts. Iodides, cyanides, and aluminium trichloride showed a slight difference in the adsorption of anions and cations, which is apparently not due to the actual process of adsorption. The adsorbability of a salt is determined by that of its component ions. Anions are adsorbed in the order $SO_4 < HPO_4$, $Cl < Br < NO_3 < I < CNS < OH$, and cations in the order K, Na, $NH_4 < Ca$, $Mg < Zn < Cu < Al < H$. A strongly adsorbable ion will supersede one possessing a lower adsorbability. J. C. D.

Adsorption by Precipitates. I. HARRY B. WEISER and J. L. SHERRICK (*J. Physical Chem.*, 1919, **23**, 205—252).—The amount to which the following anions, chloride, bromide, iodide, chlorate, permanganate, nitrate, nitrite, cyanide, thiocyanate, ferrocyanide, and ferricyanide, are adsorbed by barium sulphate has been determined. Barium sulphate was precipitated by mixing a solution of sodium sulphate with solutions of barium salts of the various acids yielding the above-named anions, and the precipitate analysed. One hundred gram-mols. of barium sulphate adsorb

0·056 equiv. ions, I'; 0·220, CNS'; 0·310, CN'; 0·831, Br'; 1·760, Cl'; 2·695, $Fe(CN)_6^{III}$; 2·847, MnO_4'; 5·837, ClO_3'; 7·467, NO_2'; 8·482, NO_3'; 13·201, $Fe(CN)_6^{IV}$. In the case of the chlorate and permanganate ions, the adsorption is less when an excess of sodium sulphate is used in the precipitation. Changes in the conditions of precipitation affect the amount of adsorption, but not the order in which the ions are adsorbed. The observed order is not in accord with Schulze's law, although the quadrivalent ferrocyanide ion is most strongly adsorbed; but there are four univalent ions more strongly adsorbed than the tervalent ferricyanide ion, and there is a wide variation in the amounts of univalent ions adsorbed. Determination of the order of the ions by direct analysis of the adsorbing phase is preferable to deducing the order from coagulation data, since the former method is superior in accuracy. It is probably inaccurate in any case to assume that the ion with the same charge as the colloidal particles has no effect in determining the critical coagulation of the colloid by electrolytes. It is more probable that the relatively small effect of the ion with the same charge as the colloid may be lost sight of altogether, because of the errors inherent in the experimental method. The order of adsorption of anions by barium sulphate is the reverse of that deduced from Hofmeister's data (*Beitr. chem. Physiol.*, 1904, **5**, 27) on the coagulation of albumin by electrolytes. The adsorption by charcoal and hydrated ferric oxide is more nearly what it is with barium sulphate. The adsorption for ions by a given adsorbent is controlled by the nature and valency of the ion. With ions of the same general character, the specific character of the adsorption is not very pronounced, and the valency factor predominates. Thus nitrate and nitrite ions are adsorbed to nearly the same extent, and among the cyanogen derivatives the order $Fe(CN)_6^{IV}>Fe(CN)_6^{III}>CN'$, CNS' is observed. Nitrates are adsorbed more than chlorates and chlorides, an observation in keeping with analytical practice. Colloidal solutions of barium sulphate are usually positive, due to strong preferential adsorption of barium ion. J. F. S.

The Congo Dyes and Adsorption as the Preliminary Phase of Chemical Union. E. Wedekind and H. Rheinboldt (*Ber.*, 1919, **52**, [*B*], 1013—1021. Compare Wedekind and Rheinboldt, A., 1914, ii, 626).—The behaviour of the blue solution obtained by treating Congo-red with acids towards various colloids has been examined; it is found that acid gels which are free from electrolytes (silicic acid, metastannic acid, titanic acid, tungstic acid, molybdic acid, vanadic acid) do not adsorb the Congo-dye acid and do not cause any change in colour on heating; basic gels, on the other hand (oxides of zirconium, thorium, aluminium, lanthanum, zinc, glucinum, iron, and chromium), adsorb the dye acid and, when heated, assume the red colour which is characteristic of the salts. It appears probable that the Congo-acid belongs to the weakest class of acids, and that aqueous solutions of Congo-

red, in consequence of hydrolysis, always contain a greater or less amount of the red, azoid, free Congo-acid, which is transformed by hydrogen ions into the blue, insoluble isomeride. The adsorption of the Congo-acid is attributed to the formation of a primary adsorption compound of the free blue acid, which when warmed or preserved becomes converted (probably through the red acid) into a complex salt of acid and base. The phenomenon thus gives an experimental confirmation of the hypothesis that, particularly in heterogeneous systems, chemical action is preceded by the production of an adsorption compound.

Similar behaviour is observed with other dyes, such as benzopurpurin 4B, benzopurpurin 10B, naphthalene-red, benzo-orange R, Congo-corinth G, and Congo-corinth B. H. W.

Osmotic Pressures Derived from Vapour Pressure Measurements: Aqueous Solutions of Cane-sugar and Methyl Glucoside. The Earl of Berkeley, Ernald G. J. Hartley, and C. V. Burton (*Phil. Trans.*, 1919, [*A*], **218**, 295—349).—The compressibility of solutions of sucrose and α-methyl glucoside has been determined in a series of concentrations at the temperatures 0° and 30°. In general, the method and apparatus adopted is similar to that used in the case of calcium ferrocyanide (A., 1909, ii, 126). The glass containing tubes, previously used, are, however, replaced by metal tubes fitted with a number of plate-glass windows, and the piezometer is divided into two limbs, thus providing for more rapid temperature adjustment. The apparatus was tested with water and mercury, and for these substances the following results were obtained: mercury, at 0°, mean relative coefficient of compressibility between 1—101 atms., $0{\cdot}169 \times 10^{-5}$; at 1·8°, mean relative coefficient between 1—110 atms., $0{\cdot}171 \times 10^{-5}$; at 29·5°, mean relative coefficient between 8—150 atms., $0{\cdot}165 \times 10^{-5}$. Water at 0·12°, absolute coefficient of compressibility between 17—48 atms., $5{\cdot}085 \times 10^{-5}$; at 30·01°, absolute coefficient between 17—48 atms., $4{\cdot}458 \times 10^{-5}$. In the case of sucrose at 0°, compressibility coefficients were obtained ranging from $4{\cdot}391 \times 10^{-5}$ for a solution containing 180 grams of sucrose per litre over the pressure range 0—20 atms., to $2{\cdot}235 \times 10^{-5}$ for a solution of 215·4 grams of sucrose in 100 grams of water over the pressure range 10—27 atms. At 30°, values were obtained varying from $3{\cdot}335 \times 10^{-5}$ for a solution of 420 grams of sucrose per litre over the pressure range 0—27 atms. to $2{\cdot}205 \times 10^{-5}$ for a solution of 243 grams of sucrose in 100 grams of water over the pressure range 88—116 atms. In the case of α-methyl glucoside at 0°, a solution of 23 grams in 100 grams of water gave the coefficient $4{\cdot}078 \times 10^{-5}$ over the pressure range 17—48 atms., and a solution of 92 grams in 100 grams of water gave the coefficient 2·893 over the pressure range 0—44 atms. At 30°, for the same solutions, the values $3{\cdot}848 \times 10^{-5}$ over the range 20—31 atms. and $2{\cdot}979 \times 10^{-5}$ over the range 24—75 atms. were found respectively. Vapour-pressure determinations of solutions of sucrose, α-methyl glucoside,

and sulphuric acid have been made at 0° and 30° in an apparatus previously described (A., 1906, ii, 599). The possible sources of error in the method of determination are discussed at some length, and in the actual experiments these are avoided or corrected in the results. Very full tabulated results are given for the three substances measured, and from the results the osmotic pressure is calculated and compared with the experimentally determined value. The calculations are made by means of the expression

$$P=\log_e[l_0/l_1-(l_0/l_1-1)\pi_0/B]\times RT/s,$$

where P is the osmotic pressure, s is the mean specific volume over the range $1-(1+P)$, l_1 and l_0 the loss of weight of the solution and solvent respectively, ρ_1 and ρ_0 the corresponding vapour densities, $\pi_{\rho'}$ and π_0 the corresponding vapour pressures, B the barometric pressure, $\pi_{\rho'}$ and π_0' the observed vapour pressures, and $[l_0/l_1-(l_0/l_1-1)\pi_0/B]=\rho_0/\rho_1=\pi_0'/\pi_{\rho'}$. The values previously published for calcium ferrocyanide (*loc. cit.*) are recalculated to allow for the "Burton correction," that the volume of the air entering the liquid is slightly different from that leaving it.

J. F. S.

The Experimental Investigation of Crystal Structure by means of *X*-Rays. R. Gross (*Jahrb. Radioaktiv. Elektronik*, 1918, **15**, 305—329).—A useful account is given of the methods which have been developed for investigating crystal structure by means of Röntgen rays. The methods described are the Bragg reflexion method, the Laue photographic method, and the Debye-Scherrer method, by means of which a crystalline powder can be examined in place of a well-developed crystal. The results which have been obtained by the last method are particularly important, as they show that substances formerly considered to be amorphous are in reality crystalline. Thus it was found that soot has essentially the same structure as graphite, and it becomes necessary to revise our opinions of the solid state. Probably there are no true amorphous solids, only crystals and liquids with varying degrees of viscosity up to the high viscosity of the glasses. E. H. R.

Kineto-electro-magnetic Theory of Crystals. J. Beckenkamp (*Verh. Physik. Med. Ges. Würzburg*, 1918, **45**, 135—163; from *Chem. Zentr.*, 1919, i, 273).—The previously described models of the constitution of the atom are reviewed and Bohr's theory is extended. The helium atom must consist of four positive nuclei which, by reason of mutual repulsion, occupy the corners of a regular tetrahedron. If each tetrahedron face contains the path of an electron, the four normals constitute magnetic axes which form an astatic system, that is, one in which no external magnetic action is exhibited at a distance. The atom itself is electrically neutralised. The lines connecting the centres of gravity of atoms united by valencies form polar electric axes. In a homogeneous regular crystal, the chemical molecules appear to be invariably arranged in a four-fold cubic lattice, the latter consisting of four

interlocked simple cubic lattices. In each of these, the electric axes of all molecules are directed towards similar tetrahedra normals. In homogeneous regular crystals, therefore, the electric axes of the chemical molecules form an astatic system. The crystalline metals, copper, silver, and gold, as well as lead and aluminium, have, accordingly, monoatomic molecules, crystalline carbon a diatomic molecule, since in the first cases the atoms are arranged in one, in the second instance in two, four-fold cubic lattices. According to this hypothesis, arsenic, antimony, bismuth, and tungsten have tetra-atomic molecules in the crystalline state. In other crystals, the astatic system may be built in two ways (two parallel and opposite axes or two axes intersecting at 120°), or in accordance with the four directions of the tetrahedra normals. This theory differs from that of Bohr, since the valency is regarded from a uniform principle, the astatic arrangement of the paths of the electron, and Bohr's axioms are deduced from general or electromagnetic laws. H. W.

Recrystallisation in Metals. G. Tammann (*Nachr. K. Ges. Wiss. Göttingen*, 1918, 1—11; from *Chem. Zentr.*, 1919, i, 321—322. Compare A., 1918, ii, 447).—During the cold working of metallic castings, planes are developed in the crystallites in which the neighbouring portions of the crystallite displace one another. In this manner, a fluid structure is attained which greatly affects the properties of the casting, particularly with regard to elasticity. The original structure returns on heating, and also the original properties. The cause of recrystallisation lies in the formation of minute new crystallites in the débris of the crystallites of the cold-worked metal; these increase very slowly at the temperature of actual commencement of the process, but with increasing rapidity as the temperature rises. If the temperature is increased in steps, each increase is accompanied by enlargement of the granules, which speedily ceases, but recommences with each new rise in temperature. An attempt is made to explain the phenomena of recrystallisation on the following lines. Two crystals in contact can only be in equilibrium with one another when crystallographically-equivalent lattice planes of both crystals lie in one plane at the surface of contact; the two space lattices must either form a single lattice or the plane of contact must be a twin plane. The two lattices must occupy a definite position with respect to one another. If one or other of these conditions is not fulfilled, new net planes of intermediate orientation are formed at the plane of contact (that is, recrystallisation begins) as soon as the temperature is raised sufficiently for appreciable change in position of the atoms or molecules in the lattice to occur. Since it is highly improbable that the contact of two crystals will occur in such a manner that a net plane of each crystal lies in one plane, recrystallisation will almost always take place at the meeting point of two crystallites. Twin formation shows that the contact of two crystals in a common plane of symmetry does not disturb the equilibrium. In twin formation,

the plane is not formed by the accidental meeting of two growing crystals, but is due to the growth of each. Twin crystals may consequently be expected to be frequently formed during recrystallisation, but the degree will vary with different metals.

Recrystallisation commences with tin after half an hour's heating at 45°; at 150°, the new particles are still relatively small. Lead behaves very similarly. With zinc, recrystallisation is distinctly evidenced at 75° by the formation of relatively large crystallites; the size of the latter decreases with increase of temperature up to 250°, and then increases, slowly at first, more rapidly from 350°. The particles are smallest between 150° and 300°. For aluminium, the minimum occurs between 300° and 500°. Observations are also recorded on rolled copper and impure tin. The unusually marked dependence of the size of the particles after recrystallisation on the degree of deformation of iron is readily interpreted by the author's hypothesis. H. W.

Eutexis and Dilute Solutions. Alb. Colson (*Compt. rend.*, 1919, **168**, 942—944. Compare this vol., ii, 186).—Starting with the law of solubility (1), $425L = T(V + \epsilon)i\,dC/dT$, the volume V of the solvent, which contains 1 mol. of the solute in saturated solution, increases with cooling when $L > 0$. It attains a minimum when L changes sign. At the eutectic point, it reaches a maximum, where it remains constant, and at the same time T and C remain constant. In other words, the solution maintains a constant composition, which is the same as that of the solid deposited. If to such a solution at a temperature equal or inferior to the eutectic temperature, Te, some of the solvent in the solid state is added, it remains in that form until the temperature rises above Te. The solubility of the solvent in the solution may be expressed by (2) $425L' = T(V' + \epsilon')i'\,dC'/dT$, and $dC'/dT = -dC/dT$. In other words, equation (1) gives the saturation of a substance A in a substance B, whilst equation (2) is relative to the saturation of B in A. The point of intersection of the two curves gives the eutectic point. W. G.

Estimation of the Size and Internal Structure of Colloidal Particles by Means of Röntgen Rays. P. Scherrer (*Nachr. Ges. Wiss. Göttingen*, 1918, 96—100; from *Chem. Zentr.*, 1919, i, 322—323).—The method of Debye and Scherrer (*Physikal. Zeitsch.*, 1916, **17**, 277) has been applied to the determination of the size and structure of typical organic and inorganic colloids. Two cases are possible, depending on the presence or absence of crystalline structure in the single colloid particle. In the former case, numerous interference figures are to be expected in the Röntgen photographs arranged in a manner characteristic of the space lattice. The position of the interference figures does not depend on the magnitude of the single crystals, but on its breadth. In the absence of crystalline structure, one or two very flat maxima in the region of the incident Röntgen ray are to be expected, and

it is then difficult to deduce evidence as to the internal arrangement of the atoms. Silver and gold particles are found to be crystalline and to show precisely the same space lattice as the macroscopic gold crystals. The size of the particles agrees with that found by other methods. Even in the smallest gold particles, which are much too small to be observed with the ultramicroscope, the characteristic space lattice is observed. Old specimens of silicic acid and stannic acid gels exhibit well-marked crystalline interference figures in addition to the characteristics of amorphous substances, and probably represent substances which are at the point of crystallising. Typical organic colloids (albumin, gelatin, casein, cellulose, starch, etc.) appear to be amorphous; the colloid particles therefore probably consist of individual molecules or of groups of irregularly orientated molecules. H. W.

Colour of Colloids. III. and IV. Wilder D. Bancroft (*J. Physical Chem.*, 1919, **23**, 154—185, 253—282. Compare this vol., ii, 102, 187).—Theoretical papers in which the discussion commenced in the previous papers is continued. III deals with the effects produced by reflection from natural objects and its influence on visibility. In IV the influence of interference and diffraction of light is considered. J. F. S.

Influence of Substitution in the Components of Binary Solutions Equilibria. XVII. Binary Solutions Equilibria of Diphenylamine with Phenols and their Derivatives. Robert Kremann and Rudolf Schadinger (*Monatsh.*, 1919, **40**, 35—56. Compare A., 1918, ii, 68, 69; this vol., ii, 15, 55, 143).—Melting-point curves have been constructed for the binary systems formed between diphenylamine on the one hand and α-naphthol, β-naphthol, pyrogallol, or one of the three dihydroxybenzenes on the other. In no case is a compound formed between the components, but only simple eutectics. This is attributed to steric influences and to a diminution of the heteropolarity. The three binary systems formed between diphenylamine and the three nitrophenols also yield only simple eutectics and no compounds. Picric acid and diphenylamine form an equimolecular compound.
J. F. S.

Influence of Substitution in the Components of Binary Solutions Equilibria. XVIII. Binary Solutions Equilibria between Nitrosodimethylaniline and some Amines. Robert Kremann and Otto Wik (*Monatsh.*, 1919, **40**, 57—79. Compare preceding abstract).—Melting-point curves have been constructed for the binary mixtures formed between nitrosodimethylaniline and α-naphthylamine, the three phenylenediamines, acetamide, benzamide, pyridine, quinoline, and acridine. It is shown that a compound, m. p. 84°, is formed between two molecules of nitrosodimethylaniline and one molecule of α-naphthylamine; *m*-phenylene-

diamine and *p*-phenylenediamine each form compounds with two molecules of nitrosodimethylaniline, whilst *o*-phenylenediamine forms an equimolecular compound, m. p. 99°. Two molecules of nitrosodimethylaniline form compounds with one molecule of acetamide and benzamide respectively. One molecule of nitrosodimethylaniline combines with four molecules of pyridine, m. p. 4·3°, whilst in the case of acridine, three compounds were formed consisting of nitroso-compound and acridine in the molecular ratios 2:1, 3:2, and 1:1. In the case of quinoline, no compounds are indicated. J. F. S.

Investigations on Carbonate- and Chloride-Fusions. Paul Niggli (*Zeitsch. anorg. Chem.*, 1919, **106**, 126—142).—The equilibrium conditions in the system Na_2O–K_2O–CaO–CO_2 have been studied between 600° and 1000° in an atmosphere of carbon dioxide at atmospheric pressure. The two binary systems Na_2CO_3–$CaCO_3$ and K_2CO_3–$CaCO_3$ have previously been dealt with (A., 1916, ii, 211). The other binary system has now been studied. Sodium and potassium carbonates form a continuous series of mixed crystals, the minimum point on the curve lying at 712° with about 46 mol. % of potassium carbonate. Mixtures of sodium and potassium carbonates containing 50 mol. % of calcium carbonate behave as binary mixtures of the two double salts $Na_2Ca(CO_3)_2$ and $K_2Ca(CO_3)_2$ below 850°, but above this temperature the salts readily lose carbon dioxide. The double salts form a continuous series of mixed crystals. Mixtures of the three carbonates containing less than 50 mol. % of calcium carbonate behave up to 900° under one atmosphere of carbon dioxide as a ternary system. The equilibrium diagram is given in the form of a triangle with the three simple carbonates as the corner constituents.

In the course of the investigation of the system Na_2Cl_2–Na_2CO_3–$CaCO_3$–$CaCl_2$, two binary systems have been examined. The examination of the system $CaCl_2$–$CaCO_3$ offers great experimental difficulties. With a large proportion of calcium carbonate, the melts become very viscous at about 700°, and the cooling effects are uncertain. Sometimes, just previous to crystallisation, an emulsion appears to be formed. Formation of oxychloride is almost unavoidable. With 30 mol. % of calcium carbonate, there is a eutectic at about 622°. The system Na_2Cl_2–Na_2CO_3 has a eutectic point at 640°. The examination of the ternary system Na_2Cl_2–Na_2CO_3–$CaCO_3$ also offered difficulties on account of the viscous nature of the melts and of the small thermal effects. Two characteristic arrest points were found, at 690° and 640°. The results are shown on a triangular diagram with Na_2Cl_2, Na_2CO_3, and $CaCO_3$ as the corner constituents. The petrological significance of the results of the investigations is discussed. E. H. R.

The Propagation of Flame in Mixtures of Acetylene and Air. Walter Mason and Richard Vernon Wheeler (T., 1919, **115**, 578—587).

Calculation of Temperatures of Explosion. A. V. Blom (*Z. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 219—221; from *Chem. Zentr.*, 1919, i, 268).—The maximum temperature obtained during explosion may be calculated from the formula: (1) $dQ = C' . dt$, where Q is the heat of combustion and is determined calorimetrically or calculated from thermochemical data, and C' the true molecular specific heat at constant volume. From the values for the specific heat of polyatomic gases obtained during recent years (the calculations of temperature, particularly for triatomic gases and the older linear formulæ, are useless), the following functions (2) for C' are obtained: H_2, $C' = 4{\cdot}70 + 0{\cdot}90 \times 10^{-3}t$; O_2, N_2, CO, $C' = 4{\cdot}90 + 0{\cdot}90 \times 10^{-3}t$; CO_2, $C' = 7{\cdot}98 + 2{\cdot}44 \times 10^{-3}t$; H_2O, $C' = 3{\cdot}84 + 4{\cdot}68 \times 10^{-3}t$. $C' = \alpha + \beta t + \gamma t^2 + \delta t^3 + \ldots$ (The temperature-coefficients express the mobility of the atoms in the molecule.) Using the general expression $C' = \phi(t) = \alpha + \beta t$, and substituting in equation (1), the formula $dQ = (\alpha + \beta t)dt$ is obtained, which, on integration, becomes $Q = \alpha t + (\beta/2)t^2$ (3). If the relative quantities of gases formed by explosion are [H], [N], [O], [CO], [CO_2], and [H_2O], the following coefficients are derived from formula (2):

$$\alpha = 4{\cdot}70[H] + 4{\cdot}90\{[N] + [O] + [CO]\} + 7{\cdot}98[CO_2] + 3{\cdot}84[H_2O],$$
$$\beta = 0{\cdot}9\{[H] + [O] + [N] + [CO]\} + 2{\cdot}44[CO_2] + 4{\cdot}68[H_2O] . 10^{-3}.$$

The temperature of explosion may then be calculated by substituting these coefficients in equation (3). H. W.

The Determination of the Temperatures Reached in Explosive Reactions. Henri Muraour (*Compt. rend.*, 1919, **168**, 995—997).—The two indirect methods commonly used for evaluating the temperatures reached in explosive reactions require the assumption of the composition of the gas at the moment of the explosion, and according as it is assumed that methane exists at the moment of the explosion or that it is formed during the cooling, so wide differences in temperature may be obtained.

Working with powders, which gave gases rich in methane, and using an "erosion" bomb with sudden liberation of the gases, the author finds that the greater part, if not the whole, of the methane contained in the products of combustion of powders is formed during the period of cooling. Thus, then, in calculating the temperatures of explosion, the most accurate results will be obtained by reverting the whole of the methane to $CO + H_2$. As a result of this, it is shown that the temperature of explosion of powders does not increase when the density of the charge is increased.

W. G.

The Thermal Decomposition of Phosphine. Max Trautz and Divacar S. Bhandarkar (*Zeitsch. anorg. Chem.*, 1919, **106**, 95—125).—The rate of decomposition of phosphine into phosphorus and hydrogen has been measured manometrically in a porcelain vessel at temperatures between 845° and 956°. Above the latter temperature, the decomposition is too rapid for measurement. The

reaction is of the first order, and is the first example of a gas reaction of this order to be recorded. Only above 945°, however, is the reaction uninfluenced by the walls of the vessel, and therefore a pure gas reaction. Above this temperature, the temperature-coefficient is about 1·8, but below 945° it sinks rapidly, owing to the growing predominance of the surface reaction. By means of the theory of gas reactions, the "heat of activation" and the size of the phosphine molecule are calculated. From the value of the former quantity, it is calculated that the limit of photosensitiveness for phosphine, apart from the infra-red, lies at about 329 $\mu\mu$. This research provides the first experimental proof of the theory of gas reactions (A., 1918, ii, 151), and also confirms the opinion that a gas reaction can be freed entirely from the influence of the surface of the reaction vessel if the temperature be raised sufficiently high.

The reaction appears to be retarded by water vapour and accelerated by copper, but the differences observed scarcely fall outside the limits of error of the experiments. E. H. R.

Catalysis. XI. The Le Chatelier-Braun Principle from the Point of View of the Radiation Hypothesis. William Cudmore McCullagh Lewis (T., 1919, **115**, 710—712).

The Atomic Ether, Hydrogen Atom, and Planck's Energy Quantum. L. Zehnder (*Ber. Deut. physikal. Ges.*, 1919, **21**, 118—125).—A theoretical paper in which the author puts forward a theory of an atomic ether. This substance is supposed to be made up of spherical ether atoms which are very small in comparison with atoms of matter; they are completely elastic, and move with a velocity comparable with that of light. A sheath of ether atoms surrounds every material atom and molecule, and all matter is pervious to ether atoms, so that there is no such state as an ether vacuum. The author is of opinion that differences in velocity of ether atoms constitute many of the physical phenomena; for example, electricity is nothing but the heat of the ether, and light, percussion of the ether. The electron is made up of a definite number of ether atoms with an increased heat content. The increase of mass of an electron with increase in velocity is attributed to the carrying of more ether atoms by the electron. This theory is examined in connexion with several physical laws, and found not to be at variance with them. The hydrogen atom is supposed to be spherical, made up of a perfectly elastic nucleus surrounded by an imperfectly elastic ether sheath. J. F. S.

Mechanical Philosophy and Surface Tension. Fred G. Edwards (*Chem. News*, 1919, **118**, 270—271).—A theoretical paper in which it is shown that the difference in thermal energy of an electron inside a liquid and a free electron may be measured by the relative energies of the positive ether atom. The energy of the positive atom of free ether is 1·058 erg., and may be calculated

by the equations $U=\frac{3}{2}pv=\frac{3}{2}(5175\times10^{17})(1\cdot39\times10^{-24})$ *C.G.S.*, $U=\frac{1}{2}mC^2=0\cdot4C^2\times10^{-24}$ *C.G.S.* From these formulæ, the velocity (C) of the ether atom is found to be $5\cdot193\times10^{10}$, or $3\sqrt{3}\times10^{10}$ cm./sec. This value is $\sqrt{3}$ times the radiation velocity, that is, tan 60° times the radiation velocity, thus proving that the path of the ether atom coincides with the four edges of a regular tetrahedron. This completes the theory of an atomic ether, previously published (*ibid.*, 1919, **118**, 183), and shows that the atom does not reciprocate in a rectilinear path, which would be the hypothetical alternative motion in a dodecahedral formation with double plena. In dilute solution, the intrinsic molecular pressure of water is found to be $4\cdot51119\times10^{11}$ dynes, which is about forty-one times larger than the generally accepted estimate. This intrinsic pressure can be exactly determined from the heat of neutralisation, so that the unknown term dp/dT of the Clausius equation ($dp/dT=L/(T[v_2-v_1])$ can be calculated. Further, if the Eötvos formula is accepted, the surface tension of a single molecule is obtainable with the weight of the molecule or molecular aggregate, and as the periodic specific volumes and periodic specific entropies of the elements are measurable, they can all be shown to be functions of the atomic shapes, which recur in accordance with the periodic system when the chemical atoms are assumed to be built up symmetrically with the ether atom as the tetrahedral unit.

J. F. S.

Theory of Allotropy: Allotropes and Allotropoids. Maurice Copisarow (*Chem. News*, 1919, **118**, 265—266).—Allotropy is defined as the capacity of an element to exist in forms differing in the mode of their intramolecular linking; it is to be regarded as a function of the valency. From this definition, it becomes possible to deduce the number of allotropes of a given element. Univalent elements can exist in only one allotropic modification, bivalent elements in two forms: (*a*) as a molecular structure in which both valencies of the elements are fixed, (*b*) as a molecular structure in which some valencies are free. In the case of tervalent elements, two allotropes are possible: (*a*) a saturated molecular structure in which all valencies are fixed, (*b*) an unsaturated molecular structure in which some valencies are free. Quadri-, quinqui-, and other multi-valent elements may exist in three allotropic modifications: (*a*) a rigid molecular form in which all valencies are fixed, (*b*) a rigid molecular form in which some valencies are free, and (*c*) a non-rigid molecular form in which some valencies are free. It thus follows that valency and the saturation or fixation of the atoms, and not the number of atoms, play the predominant part in the determination of allotropes, and consequently allotropy becomes the capacity of an element to exist in forms differing in the mode of their intramolecular structure. Molecular forms differing in the number of atoms or the distribution of linkings, but all belonging to the same type of linking, can be termed allotropoids. These molecular forms serve as the transi-

tion stage between polymorphism and allotropy, and can be compared with cryptoisomeric substances. J. F. S.

The Hollandus Writings: a Forgery in the Second Half of the Sixteenth Century. Paul Diergart (*Chem. Zeit.*, 1919, **43**, 201).—A reasoned statement showing that the works attributed to Isaak and Johann Isaak, of Holland, are forgeries of a date somewhere in the second half of the sixteenth century. J. F. S.

The Death of Scheele. Luciano P. J. Palet (*Anal. Soc. Quím. Argentina*, 1919, **7**, 44—48).—The author directs attention to an error widely disseminated in chemical and toxicological literature that Scheele died from the effects of the inhalation of hydrogen cyanide, which he discovered. The error seems to have arisen from the confusion of the following facts. In 1775 Scheele discovered hydrogen arsenide, and in 1782 hydrogen cyanide. In 1813 the toxicity of the latter gas was demonstrated by Gehlen, also a Swede, who died in 1815 from the effects of poisoning with hydrogen arsenide. Scheele died in 1786 of phthisis. W. S. M.

Loosening of Fixed Glass Parts (Stopcocks, etc.) by means of Hydrogen Peroxide. Schwarze (*Münch. Med. Woch.*, 1918, **65**, 1327; from *Chem. Zentr.*, 1919, ii, 83).—Glass stoppers, stopcocks, etc., which have become fixed may be loosened by immersion in undiluted hydrogen peroxide solution. H. W.

Device for Removing Plugs from Stopcocks. Vernon C. Allison (*J. Ind. Eng. Chem.*, 1919, **11**, 468).—The apparatus consists of a wooden vice, one jaw of which is hollowed so that it fits over the handle and presses against the wide end of the barrel of the tap, whilst the other jaw carries a pin, by means of which a steady pressure can be exerted against the narrow end of the tap. Almost any tap which has "stuck" can be loosened by using this vice. W. P. S.

Inorganic Chemistry.

The Systems Chlorine, Hypochlorous Acid, Sodium Hypochlorite. de Mallman (*Compt. rend.*, 1919, **168**, 1114—1117).—To determine the amounts of free chlorine x, chlorine as hypochlorous acid y, and chlorine as sodium hypochlorite z, in an aqueous solution containing chlorine in the three forms, the following process is recommended. The total active chlorine, a, is first determined, giving $x+2y+2z=a$, and if this is determined iodometrically, the mixture with potassium iodide being acidified with a known volume of $N/5$-hydrochloric acid, then the loss in acidity,

β, may be subsequently determined, and expressed in terms of chlorine gives $y+2z=\beta$. If, now, air is bubbled through a given volume of the original solution for five minutes, the whole of the free chlorine is removed, and may be estimated iodometrically, giving x, and thus the three unknowns may be determined. If sodium chloride is present, the value for x is slightly too high, a portion of the chlorine present as hypochlorous acid being carried over. As a result of numerous experiments, the author concludes that when chlorine, hypochlorous acid, and sodium hypochlorite in aqueous solution are mixed, there is produced, in reality, the reversible reaction $Cl_2+NaOCl+H_2O \rightleftarrows 2HClO+NaCl$. W. G.

Existence of Polythionic Chlorides in Solutions of Sulphur in Sulphur Monochloride. G. Bruni and M. Amadori (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 217—228).—The cryoscopic behaviour of sulphur monochloride in bromoform solution corresponds with the formula S_2Cl_2. A mixture of sulphur monochloride and sulphur depresses the freezing point of bromoform by an amount less than the sum of the depressions produced by the two solutes taken separately. The conclusion is drawn that such a solution contains polythionic chlorides in equilibrium with their components, the divergence of the actual from the calculated depression indicating approximately the formula of the complex chloride. In bromoform solution, the highest such complex compound definitely known to be present is the tetrathionic chloride, S_4Cl_2, but chlorides richer in sulphur probably exist in solutions of sulphur in the monochloride. To the presence of these polythionic chlorides are due the formation of polythio-derivatives by the action, substitutive in character, of sulphur monochloride on organic substances, and also the fact that, in the cold vulcanisation of caoutchouc by means of sulphur monochloride, products may be formed containing sulphur in excess of the ratio S:Cl. T. H. P.

The System SiO_2. A. Smits and K. Endell (*Zeitsch. anorg. Chem.*, 1919, **106**, 143—148).—In an earlier paper (A., 1913, ii, 318), an attempt was made to explain the system SiO_2 in terms of the authors' theory of allotropy, two pseudo-components being assumed. To account for a metastable transition point, however, the system must be at least ternary, and consequently the solution put forward in the earlier paper is incorrect. An assumption of three pseudo-components is now made, of which two are assumed to be in a state of invariable equilibrium, and are treated in the equilibrium diagram as one component. The discussion is limited to the α- and β-crystobalite portion of the system, and does not deal with tridymite. E. H. R.

Limits of Formation of Mixed Crystals between Potassium Chloride and Sodium Chloride. R. Nacken (*Sitzungsber. K. Akad. Wiss. Berlin*, 1918, 192—200; from *Chem. Zentr.*, 1919, i, 77. Compare Kurnakov and Shemtschushni, A., 1906, ii, 443).—The experiments were undertaken with the

object of investigating the separation curve with greater accuracy than has yet been possible with cooling curves, which can show considerable inaccuracies due to the tardiness with which equilibrium is established in the solid phase. The method adopted was that of Day and Sosman (A., 1911, ii, 496), and the region of existence of mixed crystals was found to be considerably smaller than has been previously assumed. The critical separation temperature lies slightly below 500° (according to previous determinations, 373—405°), the composition of the maximum at about 65 mol. % NaCl. In a mixture of the two components, pure sodium chloride appears to be stable below 300°, pure potassium chloride slightly below 250°.

Investigation of the various mixtures was carried out by the aid of their refractive indices, using suitable mixtures of liquids; the latter were made up from eugenol with either oil of cinnamon or sandal-wood oil or Bergamot oil. H. W.

Rearrangement of Acid Salts of Dibasic Acids in Aqueous Solutions into Normal (Neutral) Salts and Free Acids. II. Th. Sabalitschka (*Ber.*, 1919, **52**, [*B*], 567—584. Compare A., 1917, i, 699, 700).—Some further experiments of a more exact nature are described, demonstrating that acid salts of dibasic acids exist in solution to a greater or less extent as a mixture of normal salts and free acids.

I. *Dialysis of Aqueous Solutions.*—The diffusates of solutions of sodium and potassium hydrogen sulphates contain quantities of free sulphuric acid which indicate that about 43% or 28·3% respectively of the acid salts have been transformed in solution into mixtures of free acid and normal salts. Similarly, the diffusate of potassium hydrogen camphorate contains an excess of the normal salt, the free acid being so slightly dissociated that it cannot diffuse so rapidly as its ion.

II. *Crystallisation.*—A 32% solution of potassium hydrogen sulphate, left at 5—10° for a few days, deposits neutral crystals. A 50% solution of sodium hydrogen sulphate (salt to water, 1 : 1), left at 5—10°, gives crystals consisting of Na_2SO_4 91·754%, $NaHSO_4$ 5·867%, H_2O 2·38%. A solution of potassium hydrogen camphorate, made by dissolving 5 grams of the acid in 250 c.c. of 0·1*N*-potassium hydroxide and evaporating to 180 c.c., deposits pure camphoric acid on cooling.

III. *Precipitation with Alcohol.*—A solution of sodium hydrogen sulphate (20 grams = 17·506 grams of $NaHSO_4$, in 50 c.c.), mixed with alcohol until a turbidity just appears (200 c.c.), gives a precipitate, during two days, of pure sodium sulphate, leaving only 4·2% of the acid salt in solution. The alcohol may be recovered easily. (Compare the experiment with the potassium salt, *loc. cit.*)

IV. *Extraction of the Acid* [*Organic*] *with Ether.*—Quantitative experiments with the camphorate are described (*loc. cit.*).

J. C. W.

Electrolytic Dissociation of Sodium Iodide. Bror Holmberg (*Svensk. Kem. Tidskr.*, 1918, pp. 6; from *Chem. Zentr.*, 1919, i, 211).—The author finds that the law of mass action is strictly applicable to the ionic dissociation of sodium and potassium iodides at concentrations from $1N$ to $0{\cdot}05N$. The method of experiment is based on the fact that the velocity of racemisation of *l*-iodosuccinic acid is dependent on the concentration of iodine ions in the solution. H. W.

New Method for the Preparation of Ammonium Iodide. E. Rupp (*Apoth. Zeit.*, 1918, **33**, 406, 473; from *Chem. Zentr.*, 1919, i, 10. Compare Brocksmit, A., 1918, ii, 16).—The following is the most suitable method of preparing ammonium iodide from ammonia and iodine in the presence of hydrogen peroxide. Powdered iodine (10 parts) is shaken with official hydrogen peroxide solution (60 parts) and gradually treated with ammonia solution (30 parts), when the iodine passes into solution. If necessary, hydrogen peroxide is added drop by drop until further evolution of gas does not occur and the solution is pale yellow in colour. The filtered solution is warmed on the water-bath, when it becomes colourless; after evaporation, the salt is rubbed with a small quantity of ammonia and dried. H. W.

Ammonium Silicate. II. Ammonia and Silicoformic Acid [Dioxodisiloxane]. Robert Schwarz (*Ber.*, 1919, **52**, [*B*], 601—606. Compare A., 1917, ii, 31).—In the experiments on the solubility of silicic acid in ammonia solutions described previously, it was doubtful whether neutralisation or merely the production of a colloidal solution had occurred. It is now shown that dioxodisiloxane, made by leading trichloromonosilane vapour into water, reacts with ammonia solution just as it does with potassium or sodium hydroxide, that is, according to the equation $Si_2H_2O_3 + 4NH_4{\cdot}OH = 2(NH_4)_2SiO_3 + 2H_2 + H_2O$. The reaction is completed in about twenty minutes, and most of the silica, with which specimens of dioxodisiloxane are usually contaminated, remains as a precipitate. J. C. W.

Influence of Different Ammonium Salts on the Precipitation of Magnesium Hydroxide. E. Brunner (*Helv. Chim. Acta*, 1919, **2**, 277—279).—If the usual explanation of the influence of ammonium chloride in preventing the precipitation of magnesium hydroxide is correct, namely, that the effect is due to the mass action of the ammonium ions provided by the salt, then a less completely dissociated salt, like ammonium sulphate, would have a weaker influence. Experiments are described which prove that the reverse is the case. Under equivalent conditions, ammonia solution produces less precipitate from magnesium sulphate when ammonium sulphate is present than when the preventative is ammonium chloride, and a mixture of the two chlorides gives much more precipitate than a mixture of the two sulphates. Even in

the absence of an ammonium salt, the sulphate gives less precipitate than the chloride.

The explanation is to be found in the greater dissociation of magnesium chloride. The sulphate dissociates largely as follows: $2MgSO_4 \rightleftharpoons Mg^{\cdot\cdot} + [Mg(SO_4)_2]''$ (compare Bredig, A., 1894, ii, 226), and therefore gives fewer magnesium ions than the chloride. The addition of ammonium sulphate depresses the normal dissociation still further, which explains the great stability of cerbolite, $MgSO_4,(NH_4)_2SO_4,6H_2O$ (Jones and Caldwell, A., 1901, ii, 375).

J. C. W.

The Nature of Subsidiary Valencies. XXIII. Thermal Degradation of the Ammines of Zinc. Fritz Ephraim (*Ber.*, 1919, **52**, [*B*], 957—964. Compare this vol., 286, 287, 291).—The expected analogy between the ammines of copper and zinc has led to a study of the latter in which only a slight parallelism is observed between the two series. The following ammines have been investigated, their temperature of decomposition being placed within brackets after each number: zinchexammine chloride (57·5°), tetra-ammine (92°), diammine (not below 200°); zinchexammine bromide (62°), tetra-ammine (143°), diammine (?); zinchexammine iodide (65°), tetra-ammine (199°), diammine (?); zinchexammine nitrate (31·5°), tetra-ammine (206°), triammine (?); zinchexammine formate (−4°), tetra-ammine (51·5°), $Zn(HCO_2)_2,2{\cdot}5NH_3$ (63°), diammine (not below 100°); zincpentammine oxalate (18°), diammine (?); zinchexammine thiocyanate (0°), tetra-ammine (86°), the triammine possibly exists; zincoctammine benzoate (−3°), pentammine (21°), triammine (56°), diammine (not below 100°); zincpentammine sulphate (19°), tetra-ammine (98·5°), triammine (185°), diammine (?).

H. W.

Cryoscopic Study of Couples. Cadmium Bromide—Alkali Bromide. E. Cornec and G. Urbain (*Bull. Soc. chim.*, 1919, [iv], **25**, 215—218).—A study of the freezing-point curves of aqueous solutions of cadmium bromide with the different alkali bromides and hydrogen bromide reveals the existence in solution of double salts of the type $CdBr_2,2MBr$, where M may be hydrogen, potassium, sodium, or ammonium.

W. G.

Cryoscopic Study of Couples. Cadmium Chloride—Alkali Chloride. E. Cornec and G. Urbain (*Bull. Soc. chim.*, 1919, [iv], **25**, 218—222. Compare preceding abstract).—In the case of cadmium chloride and alkali chlorides, a cryoscopic study reveals the existence in aqueous solutions of double salts of the type $CdCl_2,MCl$, where M may be hydrogen, potassium, sodium, or ammonium.

W. G.

Lead Nitrato-Hypophosphate and Related Substances. Edmund von Herz (*Z. ges. Schiess. u. Sprengstoffw.*, 1916, **11**, 365—367, 388—389; from *Chem. Zentr.*, 1919, i, 271).—Attempts

to use phosphorus and its compounds in the manufacture of explosives have generally resulted in failure, but a highly explosive double compound, $Pb(NO_3)_2,Pb(H_2PO_2)_2$, may be prepared when lead nitrate, as source of oxygen, is mixed in the moist state with lead hypophosphite. Its rate of detonation is greater than that of mercury fulminate and approximately equal to that of lead azide. Its small energy content, or the relatively small volume of gas liberated by its decomposition (117 litres per kilo., as contrasted with 230 litres with lead azide and 314 litres with mercury fulminate), inhibits its use as initial explosive in the usual amount of charge. Its suitable sensitiveness and detonation point, its great stability, and the high temperature of its flame render it very appropriate for percussion-fuse compositions. It is prepared by adding a hot saturated solution of lead nitrate (331 grams) to a boiling saturated solution of calcium hypophosphite (170 grams), and cooling the mixture rapidly with efficient stirring, when white, crystalline lead hypophosphite separates. Two hundred and fifty grams of the latter are added with stirring to a boiling solution of lead nitrate (500 grams) in water (1·5 litres), and rapidly cooled. The double compound, dried at 40—50°, is only practically useful when it is obtained as a heavy, granular, crystalline powder; it is less suitable in the form of needles or as a felted, voluminous mass.

H. W.

New Atomic Weight Determinations. [Thorium-lead and Scandium.] O. Hönigschmid (*Zeitsch. Elektrochem.*, 1919, **25**, 91—97).—An account is given of a series of atomic weight determinations of thorium-lead and scandium. Lead from thorite was converted into chloride, and the ratios $PbCl_2:2Ag$ and $PbCl_2:2AgCl$ determined. From these experiments, the values 207·88 (one expt.) and 207·91 (two expts.) were obtained respectively. The mean value for Pb_{Th} is $207·90\pm0·013$, which is the highest value yet obtained for any variety of lead. Further experiments were also made by the same method with lead from three different samples of thiorianite of unknown origin, but probably from Ceylon. The following mean values were obtained: (1) 207·21, (2) 206·91, and (3) 206·84 for the three samples. From the results of the investigation, the author is of the opinion that a lead isotope of atomic weight 208·1 probably exists, and that in all probability Th.-*D* is not absolutely stable, but has a very long average life. The general question of the origin of the various lead isotopes is discussed, and the recent work of Soddy, Fajans, and others reviewed in this connexion. It is pointed out that the whole of the atomic weight determinations of scandium have been made by the sulphate method, and that very divergent results, fluctuating between 44·1 and 45·2, have been obtained by different investigators. The author has therefore made a series of analyses of the bromide by the Richards method. The bromide was prepared by heating the oxide in a quartz tube with carbon and bromine vapour, and the product purified by sublimation in a quartz tube. The

product was collected and treated generally in the way adopted by the author in his determinations of the atomic weights of uranium and thorium (A., 1916, ii, 484, 510). The sublimation of scandium bromide does not take place below about 1000°, at which temperature the substance has not melted. It is also found that after sublimation the quartz tube has been attacked to a slight extent by the bromide, according to the equation $4ScBr_3+3SiO_2=3SiBr_4+2Sc_2O_3$. The amount of the reaction is not great, and was determined by weighing the quartz tube before and after the experiments. A correction based on this action was introduced into the final calculations. For the purpose of reducing the weighings to vacuum standard, the specific gravity of scandium bromide was determined, and the value 3·910—3·913 obtained. Two specimens of scandium were used in the experiments: I, supplied by R. J. Meyer, and II, supplied by Sterba-Böhm. These specimens had been purified by different methods, and a spectroscopic examination by Haschek indicated that they were both absolutely pure—so pure, in fact, that the very persistent ytterbium line $\lambda=3694·37$ was not present in the spectra. Specimen I gave a mean value for the atomic weight Sc=45·105 (eight expts.), and specimen II the value Sc=45·093 (ten expts.), the mean of the whole being 45·099±0·014, a value which is rounded to 45·10, and is one unit higher than the value 44·1, at present adopted by the International Atomic Weight Committee. J. F. S.

Blue Copper Oxide. H. E. Schenck (*J. Physical Chem.*, 1919, **23**, 283—285).—A mixture of copper sulphate and aluminium containing approximately 5% of copper oxide was dissolved in water and precipitated with a slight excess of sodium hydroxide, filtered, thoroughly washed, and dried at 110°. The dried precipitate was very light blue in colour, and on grinding to a very fine powder and heating first in a Bunsen flame and then in a blowpipe flame, the colour changed to a light greyish-blue with no signs of blackening. A similar mixture containing twice as much copper oxide remained blue after heating in the Bunsen flame, but showed signs of blackening when heated in the blowpipe. The view is expressed that alumina stabilises the blue oxide of copper, and that the change from blue to black is due to an agglomeration of the particles. Similar preliminary experiments were made with other oxides; these were in all cases made with 5% of the oxide to 95% of alumina; manganous oxide is pink before heating and brown after heating; cobalt oxide is white with a blue tinge, but deep blue after heating, and nickel oxide is green before heating, but yellow after heating. J. F. S.

The Nature of Subsidiary Valencies. XX. Ammines of Cuprous and Lithium Salts. Fritz Ephraim (*Ber.*, 1919, **52**, [*B*], 236—241. Compare A., 1918, ii, 313).—The author hoped to find simple rules governing the formation of ammines by the salts of univalent metals, but has met with quite conflicting conditions

in the case of silver (*ibid.*), aurous, cuprous, thallous, and lithium compounds, as may be seen from the following summary of the properties of the haloids. Lithium salts yield tetrammines, which increase in stability from chloride to iodide. The same order of stability, with smaller and smaller differences, is met with among the tri- and di-ammines, but in the case of the monoammines the order is reversed, as it is with the silver haloid triammines. Cuprous haloids form triammines of almost identical stability, whilst aurous salts only give diammines. Thallous salts, owing no doubt to the great atomic volume of thallium, do not combine with ammonia. The lack of co-ordination with the generalisations made in earlier papers is obviously due to the fact that these were made on hexammines, which the salts of univalent metals do not form at all.

The following list records the temperatures at which the vapour pressures of the ammines are 760 mm. Triammines are formed by cuprous chloride, 46·3°; bromide (pale green), 49·3°; and iodide (almost white), 50°. Diammines only are given by cuprous thiocyanate and nitrate, whilst the cyanide only forms a monoammine. (The present results differ from Lloyd's, A., 1908, ii, 847.) Tetrammines are produced by lithium chloride, 12°; bromide, 53·8° (Bonnefoi, A., 1900, ii, 478); iodide, 90·5°; nitrate, a syrup, more stable than the chloride tetrammine; chlorate, a fairly mobile liquid; and perchlorate, a solid which decomposes and liquefies at the ordinary temperature. J. C. W.

The Nature of Subsidiary Valencies. XXII. Thermal Degradation of Ammines of Copper. Fritz Ephraim (*Ber.*, 1919, **52**, [*B*], 940—957. Compare Ephraim and Bolle, A., 1916, ii, 104).—The present communication deals mainly with the stability of the intermediate ammines of copper, and forms the first of a series of such investigations, the theoretical discussion of which is withheld pending the accumulation of more comprehensive data.

The experiments were performed by saturating the requisite salt with ammonia at a low temperature in a bulb blown at the bottom of a small Y-tube; the temperature of the ammine was then gradually raised and maintained constant at those points at which gas was noticeably evolved until evolution of gas practically ceased, the composition of the residue being deduced from the loss in weight. In general, three cases present themselves: (1) the ammine is stable up to a definite temperature, slightly above which ammonia is rapidly evolved, and the next lower ammine is formed; (2) a continuous series of solid solutions exists between two well-defined ammines; (3) the ammine yields solid solutions initially, which are suddenly discontinued, and ammonia is rapidly evolved to the next lower stage, or, conversely, a sudden evolution of ammonia is followed by the formation of solid solutions.

Cupric chloride gives the following ammines: $CuCl_2,2NH_3$, which decomposes below 270°; $3CuCl_2,10NH_3$, formed at 105° and stable to 124°, when it yields the diammine; $CuCl_2,5NH_3$, which below

105° forms solid solutions, which attain the composition $CuCl_2,6NH_3$ at about −15°. Cupric bromide yields $CuBr_2,2NH_3$, decomposing at about 260°; $3CuBr_2,10NH_3$, decomposing at 155°; $CuBr_2,5NH_3$, unstable above 116° and yielding solid solutions below this temperature, which have the composition $CuBr_2,6NH_3$ at about 0°. Cupric iodide yields solid solutions of hexammine and pentammine, which have the composition of the latter at 119·5°, when $3CuI,10NH_3$ is formed; the latter passes at 147° into the diammine. Copper sulphate gives a pentammine, which at about 99° is converted into the tetra-ammine, which slowly loses ammonia at 141·5°, forming the diammine. Copper nitrate gives a deep blue tetra-ammine, which is converted below 15° into a similarly coloured hexammine and decomposes above 205°, yielding indefinite products. Copper pentammine thiocyanate is converted into the tetra-ammine at 3°, which is stable to 101°, when gas is evolved and a series of solid solutions is formed up to 127°, at which the diammine is formed; decomposition occurs above this temperature. Copper tetra-ammine acetate is converted at about 80° into the diammine, which decomposes at about 175°. Copper pentammine oxalate is slowly converted into the diammine at about 46°; the latter is stable at 170°, but is completely decomposed at a higher temperature. Copper octammine benzoate is stable below −3°, at which temperature it is transformed into the hexammine; the latter decomposes with rising temperature, yielding solid solutions, which at 78° have the composition of the tetra-ammine; at 180°, formation of the diammine is complete, whilst at higher temperatures the material melts and decomposes. H. W.

Thallous Oxide. Alfred Kölliker (*Chem. Zeit.*, 1919, **43**, 231).—In this preliminary communication, the author disputes the statement occurring in the literature of the subject that "the greyish-black coating of oxide produced when the metal is exposed to air does not penetrate far into the metal, the latter reappearing when the oxide is dissolved in water." Thallium was prepared from thallium sulphate either electrolytically or by means of zinc, and it was found that the whole of the metal was oxidised in a little time. The thallous oxide formed goes completely into solution, and any of the thallium salts can be precipitated therefrom by the usual precipitants, a property which can be utilised for the separation and purification of thallium salts. J. S. G. T.

Cerium Nitride. P. Fabaron (*Ann. Chim. anal.*, 1919, [ii], **1**, 156).—When metallic cerium is heated in a closed copper tube, the oxygen of the air in the tube combines with the copper and the nitrogen with the cerium. The cerium nitride, CeN_2, formed has a greyish-black colour and is decomposed by water, yielding ammonia and cerous oxide. W. P. S.

The Constitution of the Ferric Salts of Hypophosphorous Acid. R. F. Weinland and W. Hieber (*Zeitsch. anorg. Chem.*, 1919, **106**, 15—45).—In addition to the previously known normal

ferric hypophosphite having the composition $Fe(H_2PO_2)_3$, a number of new basic compounds have now been prepared. It has also been found that ferric hypophosphite combines with other inorganic acids to form complex compounds containing both acid radicles, and many such compounds have been characterised and analysed. On account of the stoicheiometric relationships found between the different compounds, and of their singular properties, in particular of their remarkable stability, it has been concluded that the majority of the compounds contain the complex cation $[Fe_3(H_2PO_2)_6]'''$, which is very stable in character and is capable of forming salts both with hypophosphorous acid and with other inorganic acids. In this respect, the ferric salts of hypophosphorous acid are very similar to those of a number of monocarboxylic acids previously described (A., 1916, i, 314).

The normal ferric hypophosphite (3:9) is considered to have the constitution $[Fe_3(H_2PO_2)_6](H_2PO_2)_3$. The 3:8 basic salt is prepared in a pure state by mixing solutions of ferric chloride and sodium hypophosphite within certain narrow limits of temperature and concentration. It forms a loose, slightly red powder, and is given the constitution $[Fe_3(H_2PO_2)_6OH](H_2PO_2)_2,24H_2O$. This salt was used for preparing many of the following hetero-acid compounds. Other basic salts isolated contain metal and acid in the ratios 6:15, 3:7, and 3:6 respectively. The last salt is considered to contain a penta-hypophosphite cation, and corresponds with the formula $[Fe_3(H_2PO_2)_5(OH)_3]H_2PO_2$.

The hetero-acid compounds were prepared in a number of ways, by the action of acids on the 3:8 basic ferric hypophosphite or by the action of sodium hypophosphite or hypophosphorous acid on ferric salts. Six compounds with sulphuric acid are described, formed by the action of the acid on the 3:8 basic salt under varying conditions. These are all either acid or neutral compounds, the three simplest having the formulæ

$$[Fe_3(H_2PO_2)_6](H_2PO_2)SO_4,4H_2O,$$

$$[Fe_3(H_2PO_2)_6](H_2PO_2)_2,3SO_4,4H_2O, \text{ and}$$

$$[Fe_3(H_2PO_2)_6](SO_4H)_3,xH_2O.$$

For a full description of the others and of the methods of preparation of all the compounds, the original must be consulted. A nitrate is described, and also an explosive perchlorate, of the formula $[Fe_3(H_2PO_2)_6](ClO_4)_3(H_2PO_2) + \frac{1}{2}H_2PO_2 + 18H_2O$. The chlorides and bromides appear to contain complex anions containing iron. Of these, the most interesting is the compound

$$[Fe_3(H_2PO_2)_6][Fe(H_2PO_2)Cl_3]_2H_2PO_2,12H_2O,$$

which is readily obtained crystalline in the form of truncated octahedra of fair size by the action of concentrated hydrochloric acid on the 3:8 basic salt.

The compounds are all sparingly soluble in water, by which many of them are slowly hydrolysed, with formation of the 3:6 basic ferric hypophosphite. They are very stable to acids, and there is little tendency for the ferric iron to be reduced by the hypophos-

phorous acid—a further proof that a complex cation is present. Alkalis, alkali carbonates, and ammonium sulphide decompose them, with formation of ferric hydroxide. Their water of crystallisation is very loosely held, and is often lost on exposure to air.

E. H. R.

Crystalline Substances with Colloidal Properties. Basic Zirconium Sulphates and the Molecular State of Zirconium Sulphate in Aqueous Solution. O. HAUSER and H. HERZFELD (*Zeitsch. anorg. Chem.*, 1919, **106**, 1—8).—In aqueous solution, zirconium sulphate is generally supposed to be hydrolysed, with formation of zirconyl sulphates containing the complex anions $ZrO(SO_4)_2''$ and $Zr_2O_3(SO_4)_2''$. This view was supported by the existence of a potassium zirconyl sulphate supposed to have the composition $Zr_2O_3(SO_4)_2K_2$. It is now shown, however, that this formula does not correctly represent the composition of the potassium salt. In reality, the basic compounds formed by the hydrolysis of zirconium sulphate in aqueous solution are much more complex than has been supposed, and three such basic sulphates have now been isolated in crystalline form. Although these compounds are definitely crystalline, yet in solution their properties are essentially colloidal.

(1) The compound $\{Zr_4(SO_4)_3(OH)_{10}\}10H_2O$ appears to exist in two forms. One of these has been previously described (A., 1905, ii, 531). The other is prepared by dissolving zirconium sulphate tetrahydrate in cold water and keeping the 2% solution for several days, when the salt is deposited in the form of needles differing only from the crystals of the first form in their optical properties. The first form is not decomposed by boiling water, whilst the second loses part of its sulphuric acid.

(2) The more basic salt, $\{Zr_8(SO_4)_5(OH)_{22}\}8H_2O$, is prepared by dissolving anhydrous zirconium sulphate in five times its weight of water and precipitating with alcohol. The precipitate is then dissolved in a little warm water and dialysed, and in the course of a few days the basic salt separates in the form of very characteristic spherical crystals which do not lose their shape when dehydrated.

(3) The salt, $\{Zr_4(SO_4)_6(OH)_8\}H_4,4H_2O$, has been previously described (A., 1907, ii, 626), being there given the formula

$$2ZrO_2,3SO_3,5H_2O.$$

The new formula takes account of its acid properties and explains its ready conversion into either of the salts (1) and (2). It parts with its water very reluctantly, only four molecules being lost at 225°.

A potassium zirconyl sulphate of definite composition has been prepared by adding, drop by drop, a saturated solution of potassium sulphate to a strong solution of zirconium sulphate tetrahydrate acidified with sulphuric acid. It has the formula

$$\{Zr_4(SO_4)_5(OH)_8\}K_2.$$

The corresponding zirconyl sulphuric acid could not be isolated.

E. H. R.

Zirconium Alkali Sulphates. Arthur Rosenheim and Jacob Pinsker (*Zeitsch. anorg. Chem.*, 1919, **106**, 9—14).—Hauser and Herzfeld have shown (preceding abstract) that the crystalline basic zirconium sulphates are semi-colloidal in character, and that their composition is influenced to an unusual degree by the temperature and concentration of the solution in which they are formed. It has now been found that the composition of the double salts formed by zirconium sulphate with sulphates of the alkali metals similarly depends on concentration and other conditions. Two such compounds with ammonium sulphate have been prepared, and are now described. When to a solution of 10 grams of anhydrous zirconium sulphate in 20 c.c. of water is added a solution of 14 grams of ammonium sulphate in 25 c.c. of water and the mixture is allowed to evaporate over sulphuric acid, a double salt separates as a crystalline crust. This salt has the composition

$$[(NH_4)_4\{Zr_4(OH)_8(SO_4)_6\}],4H_2O,$$

and is evidently the ammonium salt of the zirconyl sulphuric acid described by Hauser (preceding abstract [3]) Subsequently, from the same solution separates a second salt, less basic than the first, and having the composition $(NH_4)_4\{Zr(SO_4)_4\}5H_2O$. This second salt is apparently only deposited when the acidity of the solution has been sufficiently increased by the separation of the first more basic salt. The second salt dissolves readily in boiling water, and, on cooling, the solution deposits crystals of the first salt.

The double potassium zirconium sulphate, $K_4Zr(SO_4)_4,3H_2O$, prepared by mixing strong solutions of zirconium sulphate and potassium hydrogen sulphate (Rosenheim and Frank, A., 1905, ii, 256), is now found to have a very variable content of water of crystallisation. When normal potassium sulphate is used, a more basic salt is obtained having the composition $K_4\{Zr_4(OH)_8(SO_4)_5\}8H_2O$. As in the case of the ammonium salts, the product separating from a weakly acid solution is more basic than that from a strongly acid solution. The normal double sulphate, $K_4\{Zr(SO_4)_4\}$ aq., is readily hydrolysed by water at 30°, with formation of complex basic salts, but no product of definite composition could be isolated. On account of their great solubility, basic sodium zirconium sulphates could not be isolated.

All the double salts described have, like the basic zirconium sulphates, colloidal properties. From their heated aqueous solutions, gels are precipitated by electrolytes and by dilute acids. These gels probably consist of colloidal zirconium hydroxide, and only dissolve slowly in excess of strong acid. E. H. R.

The Nature of Subsidiary Valencies. XXI. Gold Compounds. Ammines of Double Salts. Thermal Decomposition of Double Haloids. Fritz Ephraim (*Ber.*, 1919, **52**, [*B*], 241—254).—The dark brown auric bromide, $AuBr_3$, which is obtained by dissolving precipitated gold in bromine, becomes brownish-yellow in an atmosphere of ammonia, and absorbs about 9 molecules of the gas at the ordinary temperature and about

23 molecules in a freezing mixture. Cæsium auribromide resembles auric bromide very closely in its behaviour towards ammonia, and the pale yellow potassium aurichloride also forms at −18° a dark orange-red compound with about $12NH_3$, which effervesces in water with the evolution of free nitrogen.

Auric bromide has the dissociation temperature, in an atmosphere of bromine, 181°, the product being aurous bromide, which is yellow at the temperature of boiling naphthalene, but becomes darker when removed from the bath. It forms a diammine (Meyer, A., 1906, ii, 664). The vapour pressure of auric chloride reaches 760 mm. at 256·5°, but if the salt is left under about 100 mm. pressure at 225° until it acquires a pale yellow colour, that is, until it is changed into aurous chloride, and is then heated further in the atmosphere of chlorine, atmospheric pressure is again reached at 289·5°. That is to say, aurous chloride is only stable in an atmosphere of chlorine over a range of 33°. Aurous chloride diammine has the dissociation temperature 113·5°.

Potassium aurichloride melts at the temperature of boiling mercury, but cæsium aurichloride has a slightly higher m. p. At 440°, however, both salts have vapour pressures of about 350 mm.

The fact that aurichlorides and auribromides of the alkali metals behave towards ammonia exactly like the auric salts suggests that they are dissociated by ammonia into the component haloids. The question is therefore raised whether any double salts do, as such, form ammines, their tendency in this direction being in great contrast to their affinity for water. J. C. W.

The Attack of Platinum and Gold by the Alkali Hydroxides. L. Quennessen (*Bull. Soc. chim.*, 1919, [iv], **25**, 237—240).—A discussion of the results of Nicolardot and Chatelot (compare this vol., ii, 161), and of results published in *Bull. Usines guerre*, 1918, No. 17, 134, from which the author concludes that pure platinum shows the highest resistance to acid reagents, and that, whilst certain alloys of gold and palladium show a high resistance to the action of alkali hydroxides, silver vessels are the more convenient for laboratory purposes. W. G.

A New Method of Preparation of certain complex Compounds of Platinum and of its Analogues. L. Tschugaev (*Bull. Soc. chim.*, 1919, [iv], **25**, 234—237).—Potassium platinonitrite reacts with ammonia in the cold to give *cis*-dinitrodiammino-platinum (compare Tschugaev and Kiltinovic, T., 1916, **109**, 1286). The similar iodo-*compound*, $Pt,2NH_3,I_2$, may be obtained by boiling potassium platinoiodide in aqueous solution with ammonia. If the ammonia is replaced by methylamine, *di-iododimethylamino-platinum*, $PtI_2,2NH_2Me$, is obtained.

The same method may be used for preparing certain complex compounds of rhodium. Thus, if rhodium iodide is warmed in aqueous solution with an excess of ammonia, the *compound*, $RhI_3,3NH_3$, reddish-brown, microscopic prisms, is obtained.

W. G.

Recovery of Platinum and Alcohol from Potassium Estimations. A. E. Smoll (*J. Ind. Eng. Chem.*, 1919, **11**, 466—467).—The alcoholic filtrates and washings are distilled until all alcohol has been removed; platinum black and water remain in the distillation flask. The distillate is then heated under a reflux apparatus through which a current of warm water is passed so that the temperature of the escaping water is 58°. The top of the reflux apparatus is connected with a condenser, and the heating is continued until all aldehyde has been expelled, as is ascertained by testing drops of the distillate. The alcohol is finally fractionated from a small quantity of sodium hydroxide. [See, further, *J. Soc. Chem. Ind.*, 1919, 444A.] W. P. S.

Solubility of Hydrogen in Palladium Mixed Crystals. G. Tammann (*Nachr. Ges. Wiss. Göttingen*, 1918. 72—78; from *Chem. Zentr.*, 1919, i, 338).—A definite limit for the solubility of hydrogen in palladium, analogous to the limits of action of other agents on mixed crystals of gold with silver or copper (A., 1918, ii. 445, 447), is shown to exist at that region of temperature in which a change of position of the two types of atom in the palladium mixed crystal is no longer perceptible. The limit lies at ⅓ mol. Pd. Taking into account the atomic structure of the palladium mixed crystal, it appears, therefore, that the hydrogen atom can only enter and continue to oscillate at lattice axes which are parallel to the diagonals of the cube which are mainly occupied by palladium atoms. H. W.

Mineralogical Chemistry.

A Chemical Investigation of Banded Bituminous Coal. Studies in the Composition of Coal. Frederick Vincent Tideswell and Richard Vernon Wheeler (T., 1919, **115**, 619—636).

"Blue John" and other Forms of Fluorite. Bertram Blount and James Harry Sequeira (T., 1919, **115**, 705—709).

Chubutite, a New Lead Mineral. Hércules Corti (*Anal. Soc. Quím. Argentina*, 1918, **6**, 65—72).—The mineral to which the name *chubutite* is given occurs in the Gobernación del Chubut (Argentine) in radiated masses of obscure, crystalline structure. D 7·95, hardness 2·5, of a yellow colour and easily reduced to powder. Analysis gave:

Al_2O_3.	Fe_2O_3.	PbO.	$PbCl_2$.	Sb_2O_3	As_2O_3.	Insol.	Total.
0·12	0·19	83·30	14·83	0·69	trace	0·76	99·89

This leads to the the formula $7PbO,PbCl_2$. The crystalline structure appears to be tetragonal. W. S. M.

A Titaniferous Mineral from the Sierra del Pié de Palo, San Juan (Argentine). LUCIANO R. CATALANO (*Anal. Soc. Quím. Argentina*, 1918, **6**, 35—48 and 83—93).—A detailed account of the chemical analysis of the mineral in question. The formula $FeTiO_3,MnTiO_3$ is established. The mineral corresponds in composition with kibdelophane, a variety of ilmenite. W. S. M.

Analytical Chemistry.

Colorimetric Determination of the Hydrogen-Ion Concentration in Small Quantities of Solution. A. R. C. HAAS (*J. Biol. Chem.*, 1919, **38**, 49—55).—The preparation of indicator papers which may be used for the rapid estimation of hydrogen-ion concentration is described. The method yields accurate results, and is of considerable value when it is impossible to carry out the electrometric method. J. C. D.

Accuracy of Different Methods of Measuring Small Volumes of Fluid. FREDERICK WILLIAM ANDREWES (*Biochem. J.*, 1919, **13**, 37—44).—A study of the inaccuracies attendant on the methods employed for measurement of small volumes and dilutions, such as are used in serological investigations. J. C. D.

Preparation of Stable Starch and Oxalic Acid Solutions by means of Metallic Mercury. A. JUNK (*Chem. Zeit.*, 1919, **43**, 258).—The solution is treated with a few c.c. of mercury, boiled, and shaken, so that the mercury is finely subdivided; the mercury is allowed to remain in the bottle containing the solution. Such treatment prevents the growth of moulds, etc., in the solutions, and the latter may be kept for years without altering in strength, even when the bottle is opened frequently. W. P. S.

Identification of Iodine in Blood by a Microcrystallographic Method. ULRICH HINTZELMANN (*Zeitsch. physiol. Chem.*, 1919, **104**, 211—216).—The method proposed by Karfunkel (*Deut. med. Woch.*, 1912, 643), which depends on the isolation of crystals of iodohæmatin, is untrustworthy for ordinary use. J. C. D.

Modification in the Technique of Fischer's Reaction for Hydrogen Sulphide. LUCIANO P. J. PALET and AMANCIO FERNANDEZ (*Anal. Soc. Quím. Argentina*, 1918, **6**, 49—51).—On account of the inconvenience in preparing and keeping *p*-aminodimethylaniline sulphate, the following procedure is substituted.

To a drop of dimethylaniline are added 2 c.c. of water, three to four drops of a 1% solution of sodium nitrite, and five drops of 10% hydrochloric acid. The liquid is neutralised with saturated sodium carbonate solution, and the nitroso-base extracted with ether. To the ethereal solution, zinc powder and a few drops of concentrated hydrochloric acid are added. When the reduction is complete, the ether layer is decanted off, 2 c.c. of water and the solution to be tested are added, then concentrated hydrochloric acid, and a few drops of 10% ferric chloride solution. The addition of a little alcohol renders the appearance of the resulting methylene-blue more distinct. It is necessary that hydrochloric acid be present in great excess. W. S. M.

Estimation of Sulphuric Acid and Sulphates. G. Meillère (*J. Pharm. Chim.*, 1919, [vii], **19**, 296—297).—In the estimation of sulphates by precipitation as barium sulphate, the precipitate should be collected while the solution is still hot and washed with hot dilute acetic acid solution. In the case of sulphuric acid, this may be neutralised with barium hydroxide solution, using phenolphthalein as indicator, and a very slight excess of the barium hydroxide then added; the mixture is acidified with acetic acid, kept at 100° for two hours, and the precipitated barium sulphate then collected. [See, further, *J. Soc. Chem. Ind.*, 1919, July.] W. P. S.

Method for the Volumetric Estimation of Sulphates. A. C. D. Rivett (*Chem. News*, 1919, **118**, 253—254).—The method is intended primarily for works purposes, and depends on double decomposition between moist, precipitated barium oxalate and certain dissolved sulphates, whereby soluble oxalates are produced which may be titrated with potassium permanganate. [For details, see *J. Soc. Chem. Ind.*, 1919, 481A.] W. E. F. P.

Continuous Process for the Estimation of Nitrogen by Dumas's Method. Ludwig Dexheimer (*Zeitsch. anal. Chem.*, 1919, **58**, 13—19).—To avoid the necessity of cooling the combustion tube after the completion of one estimation and before another can be started, a procedure is described for removing and inserting successive boats while the tube is still hot. The essential feature consists of means for passing the current of carbon dioxide in a reverse direction through the tube while the latter is opened at one end. Provision is also made for oxidising the reduced copper when necessary. W. P. S.

The Estimation of Total Nitrogen in Soils containing Rather Large Amounts of Nitrates. R. S. Snyder (*Soil Sci.*, 1918, **6**, 487—490).—If the organic matter of the soil is within the usual average (0·8—3·0%), the Hibbard or the "mercury" methods of carrying out the Kjeldahl digestion give quite accurate

results for total nitrogen, even if 10% of the nitrogen is present as nitrate. Methods for total nitrogen, modified to include nitrate nitrogen, such as Ulsch's method, must, however, be used if the organic carbon content of the soil is lower than 0·5%. W. G.

Estimation of Nitrite and Nitrate Nitrogen in the Presence of other Nitrogen Compounds. TH. PFEIFFER and W. SIMMERMACHER (*Landw. Versuchsstat.*, 1919, **93**, 65—76).—For the estimation of the various forms of nitrogen in such substances as soil extracts, the total nitrogen other than nitric nitrogen is estimated by Kjeldahl's method, using 5 grams of ferrous sulphate. Ammonia nitrogen is estimated by distillation with magnesium oxide; after the ammonia has been removed, the residual solution is treated with 12 grams of magnesium chloride and 3 grams of finely divided copper–magnesium alloy (compare A., 1917, ii, 504), and again distilled to obtain the ammonia derived from the nitrites and nitrates. To estimate the nitrate nitrogen, 75 c.c. of the extract are boiled for one hour with the addition of 1·5 grams of dextrose, 0·3 gram of ferrous sulphate, and 5 grams of sodium carbonate; ammonia and nitrite nitrogen are thus expelled, and the solution is then distilled with copper–magnesium alloy as described. [See, further, *J. Soc. Chem. Ind.*, 1919, July.] W. P. S.

Scrubber for Ammonia Distillations. B. S. DAVISSON (*J. Ind. Eng. Chem.*, 1919, **11**, 465—466).—The scrubber or still-head described consists of a bulb of about 200 c.c. capacity provided with an exit tube at the top, through which the steam, etc., passes to the condenser, and a lower tube or stem for connecting the bulb to the distillation flask. This lower tube extends into the bulb, and is then bent downwards to nearly the wall of the bulb; the tube ends in a small bulb having three openings in the same horizontal plane. The first portion of steam which enters the bulb condenses, and the water flows down about the small bulb, there acting as a scrubbing solution for the remainder of the vapours. W. P. S.

Albuminoid Ammonia Test. EVELYN ASHLEY COOPER and JOSEPH ALAN HEWARD (*Biochem. J.*, 1919, **13**, 25—27).—Potassium permanganate may contain a stable nitrogenous impurity which cannot, as a rule, be removed by prolonged boiling with alkali. This impurity yields ammonia, particularly when the permanganate–alkali mixture is boiled in the dilute condition, and the error involved may be so great as to vitiate the value of the albuminoid ammonia test altogether. [See, further, *J. Soc. Chem. Ind.*, 1919, 438A.] J. C. D.

Identification of Arsenious Acid. Reply to Tunmann. R. WASICKY and A. MAYRHOFER (*Pharm. Post.*, 1918, **51**, 409—410; from *Chem. Zentr.*, 1919, ii, 224).—The authors do not agree with Tunmann's observations (A., 1918, ii, 453) on the

extension of microchemical methods to the detection of arsenic in pharmaceutical preparations, and, further, point out that the destruction of organic matter by concentrated sulphuric acid on the object-glass does not suffice for the detection of arsenic in all possible forms of combination. H. W.

Estimation of Boric Acid. PAUL JANNASCH and FRIEDRICH NOLL (*J. pr. Chem.*, 1919, [ii], **99**, 1—33).—Alcoholic sodium ethoxide solution is recommended for the titration of boric acid solutions in the presence of glycerol; the interfering action of carbon dioxide is thus eliminated. For the estimation of boric acid in minerals, the sample is fused with sodium phosphate and metaphosphoric acid, the boric acid distilled in the presence of methyl alcohol and phosphoric acid, and titrated after the methyl alcohol has been expelled from the filtrate. [See, further, *J. Soc. Chem. Ind.*, 1919, 411A.] W. P. S.

Estimation of Free Carbon Dioxide in Water. HARTWIG KLUT (*Ber. deut. pharm. Ges.*, 1919, **29**, 344—359).—Directions are given for the estimation of free carbon dioxide in water at the source of the latter. The titration is made with sodium carbonate solution, phenolphthalein is used as the indicator, and potassium sodium tartrate is added to the water to prevent interference by ferrous salts. W. P. S.

Estimation of Free Carbon Dioxide in Water. RUDOLF CZENSNY (*Zeitsch. anal. Chem.*, 1919, **58**, 1—12).—To ensure that the correct quantity of indicator is present, a combined solution containing 2·6525 grams of sodium carbonate and 2·5 grams of phenolphthalein is used for the titration of the free carbon dioxide. One hundred c.c. of the water are titrated with this solution; the number of c.c. used, less 0·52 c.c., is multiplied by 1·22 to obtain the mg. of free carbon dioxide per 100 c.c. of water. W. P. S.

Micro-elementary Analysis. ERNST MÜLLER and HERTHA WILLENBERG (*J. pr. Chem.*, 1919, [ii], **99**, 34—44).—A suitable apparatus is described for the determination of carbon and hydrogen in small quantities (2 to 5 mg.) of substance. The apparatus is constructed entirely of glass, rubber connexions are not used, a single burner is used for heating the combustion tube, and the oxygen is prepared from potassium dichromate and Caro's acid. W. P. S.

Efficiency of Potash Absorption Apparatus and Comparative Trials with a New Form of Helical Apparatus. J. FRIEDRICHS (*Zeitsch. angew. Chem.*, 1919, **32**, 129—132).—A new form of potash absorption apparatus for combustion analysis is described consisting of two cylindrical vessels of light glass fused one inside the other. The gas enters at the top of the inner vessel

and passes through a hole at the bottom into the annular space between the two vessels. A spiral is moulded on the outer wall of the inner vessel so that its apex leaves only a small clearance in the annular space, and the bubbles of gas emerging from the inner vessel are compelled to follow the spiral path in their passage up to the exit, whilst at the same time the displaced liquid is free to circulate through the narrow clearance between the helix and the outer vessel. At the top an exit orifice is provided, on which is fitted, with a ground-in joint, a bent calcium chloride tube. The whole apparatus, when filled, weighs only about 38 grams and contains 10 c.c. of potash solution. It is compact and not liable to breakage, the whole surface can easily be wiped clean, and if the liquid is sucked back there is ample room in the capacious inner vessel to prevent loss. The path travelled by the bubbles of gas is about 25 cm. long, and yet the resistance pressure of the liquid is equivalent to only 5 cm. The efficiency of this apparatus has been tested comparatively with a number of well-known types of other absorption apparatus with different speeds and quantities of carbon dioxide in air, and the results were most favourable.

J. F. B.

Studies of Acidosis. XIII. A Method for Titrating the Bicarbonate Content of the Plasma. Donald D. van Slyke, Edgar Stillman, and Glenn E. Cullen (*J. Biol. Chem.*, 1919, **38**, 167—178).—Blood is drawn with precautions against loss or accumulation of carbon dioxide. Two c.c. of the plasma are measured into a round-bottomed flask of 150 to 200 c.c. capacity, and 5 c.c. of 0·02*N*-hydrochloric acid are added. Carbon dioxide is removed by vigorous shaking, and titration is carried out with 0·02*N*-carbonate-free sodium hydroxide, using neutral-red or phenolsulphonephthalein as indicator until the colour of the solution matches one of known hydrogen-ion concentration. The results agree well with those given by the carbon dioxide capacity method over a range of bicarbonate concentrations (0·03—0·01*M*) ordinarily encountered in man, even in severe acidosis.

J. C. D.

Microchemical Distinction of Sericite and Talc. O. Hackl (*Verh. geol. Reichanst. Wien*, 1918, 1; from *Chem. Zentr.*, 1919, ii, 225—226).—The macrochemical distinction of sericite from talc is tedious, since the former frequently contains magnesium and the latter aluminium. The following microchemical method is proposed. A small quantity of the finely powdered specimen is boiled with concentrated hydrochloric acid in a small platinum spoon, the precipitate is allowed to subside, and the supernatant liquid is drawn off with a small pipette and evaporated in a platinum lid to remove the bulk of the acid, which cannot be neutralised, since the process involves the introduction of too large quantities of salt into the solution, whereby further concentration is hindered. The residue is warmed with a small quantity of water containing a trace

of hydrochloric acid; the undissolved matter is allowed to separate, and the clear liquid withdrawn with a capillary pipette. A drop of this solution is tested for potassium with freshly prepared platinic chloride solution, preferably using a cover-glass of quartz; a second drop is tested for aluminium by addition of cæsium chloride in the presence of sodium sulphate, which renders possible the formation of the alum. Magnesium is detected by the usual method in a third drop after precipitation of any considerable amount of aluminium by addition of ammonia; the precipitate need not be removed. H. W.

Estimation of Mercury in Mercury Salicylate. A. Costantino (*Giorn. Farm. Chim.*, 1918, **67**, 7—12; from *Chem. Zentr.*, 1919, ii, 4—5).—Mercury salicylate (0·25 gram) is warmed in a porcelain dish on the water-bath for about six minutes with concentrated sulphuric acid (2 c.c.). The solution is diluted with water to 160 c.c. and electrolysed in a platinum dish during fourteen minutes, a rotating platinum anode and a current of 6 amperes at 5 volts being used; without interrupting the current, the deposit is washed successively with water, alcohol, and ether, and dried in a desiccator. A mercury cathode may be used in place of a platinum dish, in which case the volume of the solution should not be more than 30 c.c., and the current 3 amperes at 7—10 volts. The process is more advantageous than those previously described and more convenient than those of the United States Pharmacopœia, 1916. H. W.

The Conductivity as Indicator in Titrations with Potassium Permanganate. Vicente Villumbrales (*Anal. Fis. Quím.*, 1919, **17**, 100—114).—In the titration of ferrous salts by means of permanganate solution, free acid is consumed according to the equation $2KMnO_4 + 10FeSO_4 + 8H_2SO_4 = 5Fe_2(SO_4)_3 + K_2SO_4 + MnSO_4 + 8H_2O$. Ordinarily, acid is added in great excess to dissolve the colloidal manganese oxide formed, and the conductivity of the mixture during the titration remains practically constant. In presence of insufficient acid, the conductivity falls with the addition of the permanganate solution until the oxidation is complete, and thereafter remains constant, the end-point being indicated by a sharp angle in the curve. In the oxidation of manganous salts in neutral solution by means of permanganate, acid is formed: $3MnSO_4 + 2KMnO_4 + 2H_2O = 5MnO_2 + K_2SO_4 + 2H_2SO_4$. In this case, the conductivity increases during the titration, and becomes constant on completion of the oxidation. W. S. M.

Use of Colloidal Silica in Iron Titrations. E. Dittler (*Chem. Zeit.*, 1919, **43**, 262).—The author confirms the statement by Schwarz and Rolfes (this vol., ii, 170) that colloidal silica, in the presence of manganous salts, prevents the oxidation of hydrogen chloride. [See, further, *J. Soc. Chem. Ind.*, 1919, July.] W. P. S.

Iodometric Estimation of Chromic Acid. I. M. KOLTHOFF and E. H. VOGELENZANG (*Pharm. Weekblad*, 1919, **56**, 514—524).—In the presence of sufficient acid (at least 20 c.c. 4*N*-hydrochloric acid in 100 c.c. of solution), the mixture may be titrated immediately after the addition of the reagents, even in the case of dilute chromate solutions. If insufficient acid is present, too much thiosulphate is consumed, owing to the occurrence of a side-reaction, the nature of which is not clearly ascertained, although it is shown that a possible oxidation of the hydriodic acid formed by air is not involved. The side-reaction is accelerated by sunlight, especially in presence of ammonium molybdate. Ammonium molybdate, on the other hand, retards the reaction between chromic acid and hydriodic acid. In strongly acid solutions, ferrous salts have a negative catalytic effect; in very weakly acid solutions, the effect is positive. W. S. M.

Analysis of Zirconium Minerals and Alloys. A. TRAVERS (*Chim. et Ind.*, 1919, **2**, 385—392).—The mineral is fused with sodium peroxide, cooled, and extracted with water; zirconium oxide, titanium oxide, ferric oxide, manganese oxide, rare earths, and a portion of the silica remain insoluble, whilst silica (remainder), aluminium, and phosphoric acid pass into solution. The insoluble portion is dissolved in hydrochloric acid and treated, after neutralisation, with sodium thiosulphate; the precipitate is collected, ignited, and weighed, and allowance made for the amount of silica and titanium oxide contained in it. The former is estimated by treatment with hydrofluoric acid and the latter colorimetrically after fusion with potassium hydrogen sulphate. The iron is estimated by titration with titanium trichloride solution, manganese by the persulphate method, and rare earths by precipitation with oxalic acid. Aluminium may be estimated in zirconium–iron alloys by precipitating the zirconium and aluminium together by treatment with sodium thiosulphate after the greater part of the iron has been removed by extraction with ether, and then separating the aluminium by fusion with an alkali. [See, further, *J. Soc. Chem. Ind.*, 1919, 421A.] W. P. S.

Electro-analysis of Gold without Platinum Electrodes. J. GUZMÁN (*Anal. Fís. Quím.*, 1919, **17**, 115—120).—Preliminary analyses were carried out with an iron anode and a cathode of platinum gauze. The electrolyte was prepared by dissolving about 0·1 gram of gold in aqua regia, adding 3 grams of sodium hydroxide in 20 c.c. of water, and then 10 c.c. of freshly prepared 2% potassium cyanide solution. The electrolysis was carried out with the temperature rising to 60°, with rapid agitation of the electrolyte. Voltage, 1·9. The results obtained were excellent. A slight disintegration of the iron anode observed in this procedure was avoided by evaporation of the solution of the gold in aqua regia to remove the nitric acid. The gold was removed from the cathode by electrolysis in hydrochloric acid. Analyses with a

cathode of gilded copper gauze gave defective results. Excellent results were, however, obtained with the use of a cathode of very fine copper gauze previously nickel-plated. If the gold contains copper, it was found necessary to add 1 gram of potassium cyanide more than is required for the solution of the precipitate, and to keep the voltage below 1·9. The deposit was washed first with a dilute (2%) solution of sodium sulphite, then with water, and finally with alcohol. W. S. M.

Determination of the Methane Content of Mine Gases or of the Concentration of a Gas in a Gaseous Mixture. Friedrich Krüger, Otto Reinkober, and Hans Riegger (D.R.-P. 309627; from *Chem. Zentr.*, 1919, ii, 39—40).—The process depends on the property of methane of absorbing ultra-red rays. The diminution in intensity of a beam of rays caused by absorption is measured in the usual manner by means of thermocouples, bolometer, or selenium cells. The process is also applicable to other technical mixtures of gases. H. W.

The Isolation and Characterisation of Alcohols as Allophanates. A. Béhal (*Compt. rend.*, 1919, **168**, 945—947).—The method of preparation of the allophanates consists in passing a current of cyanic acid gas into the alcohol, filtering off the product, washing it with ether, and recrystallising the allophanate from absolute alcohol, benzene, or acetone. The alcohol is characterised by the m. p. of its allophanate, and then the alcohol is regenerated and its physical constants determined. This method can be applied to tertiary alcohols. The terpenic alcohols, except linalool, behave normally in this method, as do also the cyclic alcohols, except terpineol, unless a phenolic group is present. If the phenolic group is converted into an alkyloxy- or aryloxy-group, the reaction then proceeds normally. Alcohols having an ethenoid linking, either in the cyclic or acyclic series, give normal allophanates. W. G.

Optical Activity and Quantitative Estimation of Menthol Dissolved in Eugenol and Phenol. Oscar von Friedrichs (*Arch. Pharm.*, 1919, **257**, 72—78).—Mixtures of menthol, eugenol, and phenol are used as local anæsthetics, particularly in dentistry, and a solution of menthol (40%), phenol (40%), and eugenol (20%) is described in the latest addition of the Swedish Pharmacopœia under the name "tinctura antiodontalgica." For the estimation of the menthol content, the author has determined the specific rotation, at 18°, of solutions of menthol in phenol (p=25—50), in eugenol (p=10—50), and in mixtures of phenol and eugenol (2:1, 1:1, 1:2), and has derived formulæ by which the menthol content may be directly calculated from the optical activity. H. W.

Use of Methylene-blue for the Detection of Sugar in Urine. Liebers (*Deutsch. med. Woch.*, 1916, **42**, 1197; from *Bied. Zentr.*, 1919, **48**, 81).—Six drops of the urine are treated

with 5 c.c. of 0·1% methylene-blue solution and ten to twenty drops of potassium hydroxide solution, and the mixture is boiled; if sugar is present in the urine, the blue colour fades, the rate at which it disappears depending on the amount of sugar. Other reducing substances in the urine do not interfere with the test.

W. P. S.

Estimation of Blood Sugar by the Modified Picric Acid Method. Stanley R. Benedict (*J. Biol. Chem.*, 1919, **37**, 503—504).—It is pointed out that the final acidity of the sodium picrate–picric acid solution used for removal of the blood proteins should be about 0·05—0·04*N*. If this is not ensured, the reagent may fail to precipitate the proteins satisfactorily (compare Rohde and Sweeney, this vol., ii, 84). J. C. D.

Estimation of Reducing Sugars Volumetrically by Schindler's Modification of Bertrand's Method. Bettinger (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 111—113).—Bertrand's volumetric method of determining reducing sugars (A., 1907, ii, 136), in which the precipitated cuprous oxide is dissolved in ferric sulphate solution and the liquid titrated with permanganate, has been rendered more rapid by using the same flask throughout and by replacing the filter-tube by a Gooch crucible. Reduction is effected in a conical flask, and the cuprous oxide washed quickly by decantation through a Gooch crucible provided with an asbestos pad, taking care to carry over as little of the precipitate as possible. Ferric sulphate solution of known titre is added to the precipitate remaining in the reduction flask, which is immediately connected by means of a rubber stopper and funnel with the Gooch crucible, and also with a tube leading to a filter-pump. A further known volume of the ferric sulphate solution is added to the Gooch crucible to dissolve the cuprous oxide remaining on the asbestos pad, and the liquid is drawn into the flask. After washing with warm water, the solution in the reduction flask is titrated with permanganate. J. P. O.

Behaviour of Inulin in the Animal Body. Application of the Benedict Method to the Estimation of Lævulose and Inulin. Ruth E. Okey (*J. Biol. Chem.*, 1919, **38**, 33—42).—Benedict's method for the estimation of dextrose (A., 1918, ii, 247) may be applied with success to the estimation of lævulose and of inulin. It is necessary in some cases to eliminate the disturbing influence of certain salts. J. C. D.

Estimation of Furfuroids (Furfurosans) in the Different Products of Beet-sugar Factories. II. R. Gillet (*Bull. Assoc. Chim. Sucr.*, 1918, **35**, 93—102).—In a previous paper (A., 1918, ii, 248), it was shown that in the determination of pectic substances in beet-sugar factory products by the Tollens-Councler

procedure, sucrose and hexoses in general yield a certain amount of furfuraldehyde, the quantity of which, in spite of precautions to ensure uniformity, is variable. Satisfactory results, however, are claimed to have been obtained by a preliminary elimination of the hexose sugars by fermentation, after which the liquid is distilled with hydrochloric acid and the phloroglucide precipitated and weighed in the usual manner. Operating in this way, the amount of pentosans and "pectic substances" in beet molasses, per cent. of the non-sugars present, was found to average 2·10 and 6·70 respectively. In the case of first- and second-grade sugars, the proportions were considerably higher, from which the author concludes that a large part of the so-called furfurosans or furfuraldehyde-yielding substances present in the clarified syrups are retained by the sugars when drying in the centrifugals.

J. P. O.

Filter for Use in the Estimation of Crude Fibre, etc. F. Mach and P. Lederle (*Chem. Zeit.*, 1919, **43**, 251).—A disk of fine platinum gauze (16 to 17 meshes per cm., each mesh 0·5 mm. wide) is placed on a perforated porcelain plate contained in a funnel, and asbestos fibre or pulp is introduced so as to form a layer on the gauze.

W. P. S.

Systematic Extractions with Ether. Joh. Pinnow (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 49—65).—At 15°, the distribution coefficient of glycollic acid between water and ether is 32, and of formic acid 2·4; at 26°, the coefficients are 38 and 2·5 respectively. The extraction of succinic acid, oxalic acid, malic acid, etc., from half-saturated solutions has been investigated. Lactic acid and citric acid may be separated and identified by extraction and use of the distribution coefficients. A substance which is not readily extracted may be estimated by making a series of successive and similar extractions; complete extraction is unnecessary.

W. P. S.

New Process for the Estimation of Oxalic Acid. Erwin Ott (*Ber.*, 1919, **52**, [*B*], 752—753. Compare H. Krause, this vol., ii, 203).—The quantitative decomposition of oxalic acid into carbon monoxide, carbon dioxide, and water by acetic anhydride in the presence of a trace of sulphuric acid had previously been described by the author (A., 1913, i, 1302), and had been attributed by him to the intermediate formation of oxalic anhydride; it had not, however, been adapted by him to the rapid and exact estimation of oxalic acid and its salts.

H. W.

Recovery of Ether in Fat Estimations. J. Grossfeld (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 81—82).—A considerable portion of the ether used in fat extractions remains in the extraction thimble; this portion of the solvent may be recovered if, as

soon as the extraction is completed, the thimble and its contents are transferred to a suitable apparatus and distilled W. P. S.

Detection of Acetone in Urine. Otto Mayer (*Zeitsch. physiol. Chem.*, 1919, **104**, 220—228).—A general review of the methods for detecting and estimating acetone in urine. A modification of the Legal test is described which gives a reaction with acetone present in a dilution of 1:1000. J. C. D.

Nephelometric Estimation of Acetone in Urine. G. Issoglio (*Giorn. Farm. Chim.*, 1917, **66**, 301—303; from *Chem. Zentr.*, 1919, ii, 150).—For the estimation of small quantities of acetone, the turbidity due to iodoform, and obtained by the use of alkaline iodine–potassium iodide solution, is compared with that given by a similarly treated solution of acetone (0·01%). The tests are performed in two similar crystallising dishes 7 cm. in diameter and 4 cm. high. Urine (100 c.c.) is mixed with half its volume of water, and 100 c.c. of the distillate are collected. The distillate (10 c.c.) is mixed with sodium hydroxide solution (5%, 10 c.c.) and water (30 c.c), and iodine–potassium iodide solution (5%, 10% KI, 5 c.c.) is added. The turbidity obtained is compared with that simultaneously given by 10 c.c. of acetone solution (0·01%). If the acetone content of the distillate is greater than that of the control, a proportionately smaller volume is taken, which is then diluted to 10 c.c.: in the reverse case, less of the control solution is taken, but the volume of the samples must invariably be made up to 10 c.c., so that the volume of solution in the dish always amounts to 50 c.c. It is observed that the rapidity with which the turbidity appears is, within certain limits, proportional to the acetone content. H. W.

Estimation of Urea in Urine by Direct Nesslerisation. Otto Folin and Guy E. Youngburg (*J. Biol. Chem.*, 1919, **38**, 111—112).—The preparation of a urease product is described, the use of which permits urea nitrogen to be determined directly by Nesslerisation. J. C. D.

Rapid Method for the Estimation of Urea in Urine. James B. Sumner [with Aaron Bodansky] (*J. Biol. Chem.*, 1919, **38**, 57—61).—To 1 c.c. of urine in a centrifuge tube is added 1 c.c. of a phosphate solution and urease. The reaction is assisted by maintaining the tube warm for twenty minutes. The proteins are then removed by potassium mercury iodide and centrifugalisation, and the ammonia estimated in an aliquot part of the supernatant fluid. The method gives results which agree well with those carried out by the aeration method. J. C. D.

Estimation of Urea and Non-Protein Nitrogen in Blood and Tissue by Means of Nessler Reagent. A. Grigaut and Fr. Guèrin (*J. Pharm. Chim.*, 1919, [vii], **19**, 233—243, 281—294).—From 1 to 3 c.c. of blood, serum, etc., is mixed with

2 to 6 c.c. of a suspension of 1 gram of soya-bean flour in 100 c.c. of water containing 0·4 gram of sodium dihydrogen phosphate; the mixture is kept at 56° for fifteen minutes, then treated with its own volume of 20% trichloroacetic acid, filtered, and the ammonia is estimated in the neutralised filtrate by means of Nessler reagent; the quantity of ammonia found is a measure of the urea present. To estimate non-protein nitrogen, the substance (blood, tissue, etc.) is thoroughly macerated and extracted with chloroform water, the extracts are treated with trichloroacetic acid to precipitate proteins, and, after filtration, a portion of the filtrate is digested with a mixture of phosphoric acid, three parts, and sulphuric acid, one part, and containing one-fifteenth of its volume of 10% copper sulphate solution. The ammonia formed is then estimated directly in the neutralised solution by means of Nessler reagent. W. P. S.

Analysis of Mercury Fulminate. A. Langhans (*Zeitsch. anal. Chem.*, 1918, **57**, 401—445).—A method described for the estimation of mercury fulminate depends on the formation of hydroxylamine when the fulminate is dissolved in 12% hydrochloric acid; the hydroxylamine is estimated by boiling the hydrochloric acid solution with the addition of iron alum solution, and then titrating the hot mixture with *N*/20-permanganate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, 389A.] W. P. S.

Tungstic and Molybdic Complexes as Precipitants of Organic Bases. Luis Guglialmelli (*Anal. Soc. Quim. Argentina*, 1918, **6**, 57—64).—Solutions of the sodium salts of the following acids in dilute hydrochloric acid were prepared: tungstic, arsenotungstic, silicotungstic, phosphotungstic, molybdic, arsenomolybdic, phosphomolybdic, arsenotungstomolybdic, arsenovanadotungstic. The effects of these reagents on the following organic bases in dilute hydrochloric acid solution were observed and tabulated: α- and β-naphthylamine, benzidine, antipyrine, pyramidone, caffeine, pyridine, nicotine, quinoline, cinchonine, cocaine, auramine. W. S. M.

A Reaction of Aconitine. L. P. J. Palet (*J. Pharm. Chim.*, 1919, [vii], **19**, 295—296).—Crystallised aconitine yields a violet coloration when heated with phosphoric acid solution (D 1·7); amorphous aconitine gives a grey coloration with the test. Both forms of aconitine give a violet coloration if the phosphoric acid is mixed previously with 4% of its weight of sodium molybdate. Aspidospermine and veratrine also give a violet coloration under these conditions, but the former may be identified by the action of oxidising substances on it, and the latter by means of its reaction with mineral acids. Other alkaloids do not give a violet coloration. [See, further, *J. Soc. Chem. Ind.*, 1919, July.] W. P. S.

Detection of the Poisons which can be Extracted with Ether from the Acid Aqueous Solution in the Stas-Otto Process. III. O. TUNMANN (*Apoth. Zeit.*, 1918, **33**, 443—444, 447—448, 454—455; from *Chem. Zentr.*, 1919, ii, 42—43. Compare A., 1918, ii, 139).—*Colchicine.*—The residue, obtained according to Stas-Otto, is an amorphous, brownish-yellow mass with a very bitter taste. The sublimates are dull white or yellow and amorphous. Hydrochloric and sulphuric acids colour the sublimate yellow. The solution in sulphuric acid becomes pale green, blue, and violet on addition of a little nitric acid. Nitric acid gives a violet, greenish-yellow, and yellow coloration, which becomes red on addition of alkali. Phenol solution causes the separation of minute drops from the aqueous solution of the sublimate. Ferric chloride imparts a dark green or olive-green colour, but only dissolves the sublimate when warmed, the coloration becoming more intense.

Caffeine can be immediately sublimed from all its pharmaceutical preparations, and also from blood or urine; it is more difficult, and often not directly possible, to obtain similar sublimates from theobromine. Caffeine sublimates consist of needles and prisms with direct extinction, and six-sided platelets; theobromine sublimates never exhibit these large crystals, but are composed of needles and masses of small nodules. If the sublimates are moistened with nitric acid (5%) and a drop of silver nitrate solution (5%) is added, large, rounded nodules, from which fine, bent crystal threads project, are observed with caffeine, whilst theobromine yields large sheaves and tufts composed of long, colourless, rectangular rods, which have oblique extinction and polarise strongly in all colours. The reaction with mercuric chloride can also be applied to theobromine; the crystals of theobromine mercuric chloride polarise in colours, generally have oblique extinction, but are composed of small groups which cannot always be recognised even with a lens. Mercuric chloride and gold chloride are not suitable reagents for distinguishing between caffeine and theobromine. With bromine–potassium bromide, crystals differing from those described by Eder (A., 1917, ii, 346) can be obtained if the caffeine sublimate is first dissolved in the bromine–bromide solution and hydrochloric acid is carefully added; in addition to a few needles (10—20 μ), single, yellow crystals separate, round which prisms gradually group themselves. All the crystals are more or less colourless after an hour. Under these conditions, theobromine does not give a precipitate. When caffeine or theobromine sublimates are treated with hydriodic acid and the solutions warmed until gas commences to be evolved, a portion of the bases collects in black lumps, whilst the remainder passes into solution; small, blackish-brown rhombs and four-sided plates separate from the caffeine solution, which appear red between crossed Nicols, show very faint pleochroism, and finally unite to irregular masses. From the theobromine solution, much larger, flat, four-sided or rhombic platelets crystallise, which show unusually marked

pleochroism and, generally, oblique extinction. Caffeine and theobromine are most readily distinguished by means of nitric acid. If the sublimates are warmed with concentrated nitric acid until a colourless rim is formed, caffeine nitrate separates in the same form as by sublimation or can be identified as chloralcaffeine, whilst the theobromine nitrate appears in short, thick crystals and rhombs which grow to masses and rosettes. The murexide test can readily be performed on an object-glass, and the results are conclusive with 20 μg., and probably with less.

Mercuric Chloride.—To avoid confusion with the members proper of this group, the following reactions for mercury may be performed with the sublimates. Zinc chloroiodide gives a pale red colour at the edges, and the precipitate is soluble in an excess of the reagent. Hydriodic acid gives a brownish-red precipitate at the rim, which is immediately soluble in excess of the reagent. Nitric acid yields a colourless solution which, on evaporation, deposits long prisms of mercuric chloride. Identification of mercuric chloride is confirmed by the following tests: Precipitation of the iodide from iodine solutions by means of copper sulphate, precipitation of the oxide by alkali, amalgamation with copper wires under a coverslip, distillation, and conversion of the distilled mercury into the iodide. H. W.

Use of Certain Reagents for the Detection of Emetine in Human Urine. Ch. Mattei (*Compt. rend. Soc. Biol.*, 1918, **81**, 315—317; from *Chem. Zentr.*, 1919, ii, 326).—The sensitiveness of a number of reagents has been determined, using emetine solutions of known content. Tancret's reagent gives a perceptible turbidity with 0·0000125 gram emetine hydrochloride in 5 c.c., Mayer-Valser's reagent with 0·000025 gram in 5 c.c., Dragendorff's and Bouchardat's reagents with 0·00005 gram in 5 c.c. Calcium chloride and hydrochloric acid give a distinct coloration with 0·0002 gram in 5 c.c. Froehde's reagent is also very sensitive. H. W.

Detection of Nicotine. O. Tunmann (*Apoth. Zeit.*, 1918, **33**, 485—486; from *Chem. Zentr.*, 1919, ii, 227).—A few crystals of *p*-dimethylaminobenzaldehyde are dissolved in a drop of fuming hydrochloric acid on an object-glass and brought into contact with a drop of an aqueous solution of nicotine. A pink, and then a reddish-violet, zone is formed at the line of contact, and the whole liquid becomes reddish-violet. The coloration increases in intensity and is permanent for ten to twenty-four hours. Under similar conditions, coniine, pyridine, and acetone do not yield colorations. Coniine, pyridine, and the other alkaloids do not influence the reaction. Aniline, in not too dilute solution, gives a red coloration, but crystals of the dye immediately separate. The reaction affords the most sensitive test for nicotine without using a microscope, and occurs within a minute with 0·2 mg. of the alkaloid. The presence of nicotine in cigar smoke is easily demonstrated in this manner.

The most sensitive microchemical reagent is a cold saturated solution of picric acid to which 10% of concentrated hydrochloric acid has been added. A yellow, amorphous precipitate, from which crystals separate in a few seconds, which is recognisable with the naked eye, is obtained with 10 μg. nicotine. With 5 μg. of the alkaloid, the precipitate is not formed, but the same crystals appear, generally, however, in indistinct, feathery forms, but always of the same magnitude and arranged in groups. The latter can generally be recognised by the eye, invariably with a lens. The limit of sensitiveness (in two to three minutes) is 3 μg. The prismatic crystals shine yellow and green between crossed Nicols, and generally have oblique extinction. Aniline, coniine, and dilute pyridine do not yield crystals. Pure pyridine gives similar crystals, but not the preliminary amorphous precipitate.

H. W.

Identification of Bilirubin. E. Klaften (*Wien. klin. Woch.*, 1918, **31**, 1018; from *Chem. Zentr.*, 1919, ii, 152).—Methylene-blue solution (1%, five drops) is added to the urine (5 c.c.), giving an emerald-green coloration, which disappears on addition of two to three drops of potassium permanganate solution (1%) and is replaced by an intense blue colour. The reaction is characteristic of bile pigments, and depends on their ready decomposition by potassium permanganate, whereby the yellow components are removed from the mixture of dyes. H. W.

A System of Blood Analysis. Otto Folin and Hsien Wu (*J. Biol. Chem.*, 1919, **38**, 81—110).—An attempt to combine a number of different analytical procedures into a compact system of blood analysis so that estimations of non-protein nitrogen, urea, creatinine, creatine, uric acid, and sugar may be carried out on 10 c.c. of blood. The pivotal point is the preparation of a satisfactory protein-free filtrate from the blood. For this purpose, tungstic acid was found highly satisfactory, less than 1 gram being sufficient to remove the proteins of 10 c.c. of blood. The separation is rapid and does not involve any loss of the substances which it is desired to estimate. In this filtrate, total non-protein nitrogen is determined by a slight modification of the direct Nesslerisation method (A., 1916, ii, 573). Sugar is estimated by the reduction of an alkaline copper tartrate solution, followed by the measurement of the depth of colour produced with Folin's phenol reagent (A., 1912, ii, 1012). The results indicate that this method is the most accurate of any proposed for the estimation of blood sugar.

J. C. D.

General and Physical Chemistry.

Optical Properties of Magnesium Platinocyanide. P. Gaubert (*Bull. Soc. franç. Min.*, 1917, **40**, 177—182; from *Chem. Zentr.*, 1919, i, 509).—The author has redetermined the optical constants of magnesium platinocyanide, $MgPtCy_4,7H_2O$, since the data recorded in the literature are discordant. The following indices of refraction are found for the usual lines: $B(687)=1{\cdot}5546$, $C(653)=1{\cdot}5585$, $D(589)=1{\cdot}5608$, $E(527)=1{\cdot}57$. H. W.

The Modifications Produced in the Spark Spectra of Different Metals by the Surrounding Medium. Bouchetal de la Roche (*Bull. Soc. chim.*, 1919, [iv], **25**, 305—309).—Spark spectra between metallic electrodes in oxygen or oxidising gases, such as carbon dioxide or nitrous oxide, are similar to those obtained in air and undergo the same change when a self-induction coil is introduced into the circuit. The spectra in reducing gases, such as hydrogen, illuminating gas, etc., are different, being very poor in rays, and if the self-induction coil is introduced, the metallic spectrum is still further enfeebled. This phenomenon varies in intensity with the metals examined, and the author gives the principal rays which persist in a number of metallic spectra in hydrogen or hydrocarbons. W. G.

Series Spectrum of Helium. A. Landé (*Physikal. Zeitsch.*, 1919, **20**, 228—234).—A mathematical paper in which relationships between the structure of the helium spectrum and the series spectra are discussed. J. F. S.

Regularities in the Spectra of Lead and Tin. R. V. Zumstein (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 59—63).—An examination of the lead spectrum shows that there are five series of three lines, the corresponding members of which have constant frequency difference, the heads of these series being the lines 7229·30, 4057·97, 3683·60, 3639·71, and 2833·17. Similarly, tin shows five groups of three lines each with constant frequency difference, the heads of each group being the lines 3801·16, 3175·12, 3009·24, 2863·41, and 2840·06. W. G.

New Lines in the Extreme Ultra-violet of certain Metals. D. S. Ainslie and D. S. Fuller (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 65—78).—The vacuum arc spectra of lead, tin, iron, nickel, cobalt, thallium, copper, aluminium, zinc, and carbon have been studied from λ 2400 to λ 1400. The vacuum arc spectra obtained for copper, zinc, and aluminium were found to correspond with the results obtained for the spark spectra. The results obtained for tin, lead, and thallium between λ 2400 and λ 1800

agree fairly well with those obtained by Saunders (compare *Astr. Phys. J.*, 1913, **43**, 234). Several new lines between λ 1800 and λ 1400 were observed and measured. W. G.

Arc Spectrum of Scandium. Sir William Crookes (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 438—439).—The arc spectrum of scandium, from wiikite has been photographed and the lines measured. The arc was produced between poles made by compressing a mixture of silver powder and scandium oxide. On the same plate, photographs were obtained of (i) iron, (ii) scandium and silver, and (iii) silver. In this way the silver lines were eliminated and the wave-length of the scandium lines deduced from the iron lines. A table is given containing 101 lines between λ 2420·025 and λ 6305·7. A photograph of the spectrum is reproduced in the paper. J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. Deslandres (*Compt. rend.*, 1919, **168**, 1179—1185). —Based on the formula

$$\nu = \pm f(n^2p^2)(m+\alpha)^2/2 + B(n+\beta)^2/2 - C(p+\gamma)^2/2 \pm K$$

(compare this vol., ii, 206), the author indicates a new method for classifying band spectra. W. G.

The Absorption Spectra of the Nitric Esters of Glycerol. Harry Hepworth (T., 1919, **115**, 840—847).

Researches on Pasteur's Principle. F. M. Jaeger (*Rec. trav. chim.*, 1919, **38**, 171—316).—This paper contains a full, detailed account of the author's crystallographic and optical researches on those complex metallic salts which can be separated into *d*- and *l*-optically active isomerides (compare A., 1915, i, 867; ii, 399; 1918, i, 3, 7; this vol., i, 5, 8, 252). The salts described fall into three groups: (1) complex salts of tervalent chromium, cobalt, and rhodium with three molecules of ethylenediamine; (2) complex salts of iron, chromium, cobalt, rhodium, and iridium with three radicles of oxalic acid; (3) analogous salts of iron, chromium, and rhodium with three radicles of malonic acid. The existence of geometrical enantiomorphism in these salts is explained by Werner's octahedral distribution of the three similar bivalent radicles about the central metallic atom, and it is pointed out that, although the optically active molecules are dissymmetrical, they are not asymmetrical, but contain certain elements of symmetry, among others a three-fold axis, which sometimes also appears in the actual crystals. The optical rotatory power of these salts is often extremely high. There appears to be no direct connexion between the optical rotation and the appearance of enantiomorphous hemihedral forms on the crystals. These forms usually appear in the derivatives of oxalic and malonic acids, but rarely in those of ethylenediamine. It is concluded that the magnitude and the intensity of the rotatory power of the dissymmetrical molecules

are not dependent on chemical contrast among the substituents distributed around the central metallic atom, but that the appearance of enantiomorphous hemihedral forms is favoured by such contrast. E. H. R.

The Phenomena of Luminescence accompanying the Oxidation of Potassium or Sodium. G. Reboul (*Compt. rend.*, 1919, **168**, 1195—1196).—The author finds that the presence of moisture is essential to the luminescence, which really accompanies the formation of the hydroxides of the metals from the oxide. W. G.

Cause of the Sensitiveness of Chemical Compounds to Light. Joh. Plotnikow (*Chem. Zeit.*, 1919, **43**, 321—323, 337—338).—A theoretical paper in which it is shown that photochemical reactions take place according to the schemes: (i) acids, $R{\cdot}CO_2H \longrightarrow RH + CO_2$; (ii) aldehydes, $R{\cdot}COH \longrightarrow RH + CO$; (iii) alcohols, $R{\cdot}CH_2{\cdot}OH \longrightarrow RH + CO + H_2$; (iv) ketones, $R{\cdot}CO{\cdot}R' \longrightarrow R{\cdot}R' + CO$; (v) diazo-compounds, $RN_2R' \longrightarrow R{\cdot}R' + N_2$. The illumination of a double bond leads either to the production of a stereoisomeride or an intramolecular change or the formation of a saturated closed ring system. Light has the tendency to convert unsaturated systems or compounds into systems stable to light. The production of stereoisomerides or intramolecular changes is to be regarded as the first intermediate stage of the action of light. Systematic photolysis and careful choice of the source of light will effect the above-named changes in all aliphatic compounds of the types mentioned. In these changes energy may be either absorbed or evolved. If there is no possibility of the formation of a more saturated or less saturated system, then a photo-equilibrium is set up which may be displaced in either direction by varying the wave-length of the light. The photochemical and photocatalytic properties of the elements are periodic functions of their atomic weights. J. F. S.

Limiting Absorption Frequencies of Röntgen Rays by the Heavier Elements particularly the Rare Earths. Manne Siegbahn and Edv. Jönsson (*Physikal. Zeitsch.*, 1919, **20**, 251—256).—The limiting absorption frequency is absolutely characteristic of a chemical element, and therefore serves to identify and establish the purity of any given element. The present work was undertaken with the object of measuring this factor in the case of the rare earth metals. Various methods were available, but for various reasons were unsuitable; the methods due to de Broglie (A., 1916, ii, 509) and Wagner (*Bayr. Akad. d. Wiss.*, March, 1916) are associated with a fundamental error due to the penetration of the Röntgen rays into the crystals, whereby the reflection occurs deep in the crystal. The authors have developed a modification of this method. The light passes through a thick lead slit at the back of which the element in any of its compounds is placed;

thence the rays pass to a rock salt or calcite crystal 2 mm. thick, and are there reflected through a second slit which is fitted with gold edges, and thence through a third slit to the photographic plate. The apparatus is fitted up in a lead-lined cast-iron chamber. The Röntgen rays were produced from a glowing cathode tube. Measurements were made with the elements of atomic numbers 48—67, 78—83, 90, and 92. The following values were obtained; the atomic number is bracketed in each case: Cd (48), $\lambda=1\cdot470$; Sn (50), $\lambda=1\cdot537$; Te (52), $\lambda=1\cdot606$; I (53), $\lambda=1\cdot641$; Cs (55), $\lambda=1\cdot706$; Ba (56), $\lambda=1\cdot739$; La (57), $\lambda=1\cdot772$; Ce (58), $\lambda=1\cdot807$; Pr (59), $\lambda=1\cdot843$; Nd (60), $\lambda=1\cdot878$; Sa (62), $\lambda=1\cdot948$; Eu (63), $\lambda=1\cdot983$; Gd (64), $\lambda=2\cdot018$; Dy (66), $\lambda=2\cdot088$; Ho (67), $\lambda=2\cdot125$; Pt (78), $\lambda=2\cdot518$; Au (79), $\lambda=2\cdot561$; Hg (80), $\lambda=2\cdot601$; Tl (81), $\lambda=2\cdot647$; Pb (82), $\lambda=2\cdot687$; Bi (83), $\lambda=2\cdot725$; Th (90), $\lambda=2\cdot979$; and U (92), $\lambda=3\cdot089$. The wave-lengths are all given in Ångström units. The results are compared with those of de Broglie (*loc. cit.*), Wagner (*loc. cit.*), and Blake and Duane (*Phys. Rev.*, 1917). J. F. S.

The Relation between the *L*-Series of *X*-Ray Spectra and the Atomic Weight. F. Kirchof (*Physikal. Zeitsch.*, 1919, **20**, 211—214).—The product of the *L*-wave-length into the square of the integer nearest approaching half the atomic weight (called Rutherford's ordinal number) is approximately a constant, equal to 12,550, for the elements from zinc to uranium. F. S.

The Radioactivity of the Natural Gases of Canada. John Satterly and J. C. McLennan (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 153—160).—The authors have measured the amount of radium emanation per litre of gas and the helium and nitrogen content of a considerable number of natural gases of Canada. The results show that there is no direct relationship between the radioactivity and either the helium or the nitrogen content, but that helium and nitrogen usually vary together.

W. G.

The Radioactivity of Rubidium. Otto Hahn and Martin Rothenbach (*Physikal. Zeitsch.*, 1919, **20**, 194—202).—The β-activity of rubidium preparations of various ages since preparation show no variation such as is to be expected if the β-rays arose from a relatively short-lived isotope of rubidium, and cannot be separated or affected by chemical purification. The radioactivity appears to be an atomic property of rubidium. The radiation from a plate 25 cm. in diameter, covered uniformly with the rubidium preparation, was compared with that of uranium from a similar surface of uranium oxide of about 0·5 mg. per cm.^{2}, α-rays being absorbed by passage through 0·01 mm. of aluminium foil. The soft β-rays of uranium-X_1, after subtracting the effect due to the penetrating β-rays of uranium-X_2, were half absorbed in 0·015 mm.

of aluminium ($\mu_{Al}=463$[cm.]$^{-1}$). The β-rays of rubidium were exponentially absorbed, showing that they were homogeneous as regards velocity and penetrating power, being half-absorbed by 0·020 to 0·0225 mm. of aluminium ($\mu_{Al}=347$—308[cm.]$^{-1}$), and are therefore somewhat the more penetrating. The soft β-rays given by radium itself have an absorption coefficient of 312(cm.)$^{-1}$ in aluminium. The velocity of the rubidium rays, estimated from their absorption coefficient, is 58 to 60% of that of light.

Under the conditions described, 12·6 grams of rubidium sulphate spread over 500 cm.^{2}, compared with a similar surface of 0·28 gram of uranium oxide, gave an activity per gram of rubidium salt 1/184th of that per gram of uranium oxide (total β-rays). Referred to the metals, the ratio is 1:139, and subtracting for the effect of the hard β-rays of uranium-X_2, the ratio is 1:32. By using less and less rubidium salt and extrapolating to a film of zero thickness, the ratio is further increased in favour of the rubidium to 1:15, to an accuracy of 20%. That is, the β-activity of rubidium is 1/15th of that due to uranium-X_1 in the same weight of uranium, absorption in the material being corrected for. For thorium, the ratio is probably 1/10th, comparing similar β-rays.

Applying the law of radioactive change, the product of rubidium should be an isotope of strontium, and of potassium an isotope of calcium. The investigation of the atomic weight of calcium derived from potash felspar, containing only small amounts of calcium, is suggested, as if the calcium is a product of the potassium, its atomic weight should be about a unit less than the accepted value. The period of half-change of rubidium, calculated from the ratio of its β-activity to that of uranium-X_1, is about 10^{11} years, and for potassium probably three times as great. If the age of the oldest felspars is taken as 10^9 years, only 0·17% of the potassium should have changed into calcium. The period of potassium, however, may be as great as seven times that of rubidium, and it is doubtful if the expected difference of atomic weight would be detectable. Similarly for the possible case of cæsium transforming itself into barium, though no β-activity of cæsium has been detected, an examination of the cæsium mineral pollux is suggested. F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes ? F. H. Loring (*Chem. News*, 1919, **119**, 14—16).—Assuming that those elements the atomic weights of which are not whole numbers are mixtures of two isotopes the atomic weights of which are whole numbers, it is suggested that the proportions of the two isotopes in the element may determine its electrical conductivity. It is further suggested that in those elements having a high conductivity there may be a greater proportion of the isotope of lower atomic weight, whilst in the non-conducting elements the proportions may be reversed. This idea is developed in a table, in which, for a number of conducting and non-conducting elements, the atomic weights and proportions of hypothetical isotopes are given. E. H. R.

New Process for Measuring the Specific Inductive Power of Liquids. FÉLIX MICHAUD and AHMED BALLOUL (*Ann. Physique*, 1919, [ix]; **11**, 295—322).—The apparatus consists of a cylindrical condenser with a vertical axis; between the armatures of which the liquid rises under the action of the electric field, this rise being shown by a lowering of the level of the liquid in a lateral glass tube. The specific inductive powers of benzene, vaselin, *cyclo*hexane, and turpentine were measured by this method, the results for benzene being 2·28 and for *cyclo*hexane 1·87. Solutions of phenol in benzene were also examined, and it was found that the dielectric constant reaches a maximum at a concentration of 11% of phenol. With mixtures, the phenomenon of "electro-osmosis" may occur, and it is proposed to study this in detail. The apparatus, slightly modified, may be used as an electrometer.

W. G.

Characteristics of the Spark Discharge and its Effect in Igniting Explosive Mixtures. CLIFFORD C. PATERSON and NORMAN CAMPBELL (*Proc. Physical Soc. London*, 1919, **31**, 168—228).—The object of the work described in the paper was to determine the relationship between the electrical characteristics of a spark discharge and its power of igniting explosive mixtures. An attempt was made to produce a form of discharge in which the current and the duration of the discharge could be controlled and varied. This failed; the discharges obtained always consisted of a discontinuous series of individual sparks, each of which lasted for a time which could not be subdivided. Quantitative measurements show that each of these individual sparks consists in the passage of a definite quantity of electricity, Q, across the gap, and represents the discharge of a condenser of definite capacity previously charged to the spark potential of the gap. The maximum duration of a spark is of the order 0·00005 second, but there is reason to believe that the actual value is considerably less than this figure. It was found impossible to obtain a discharge which was continuous, except when it took the form of an arc or a brush. The sparks obtained from an induction coil are of the same type as those obtained from a condenser. It is therefore suggested that the quantity Q, together with the form of the spark gap, may be sufficient to define the nature of the spark and to determine its igniting power. It is shown that discharges which consist of a series of similar sparks have the same igniting power as a single spark of the same character; that is to say, that the ignition, if it occurs at all, occurs at the first spark. Working with mixtures of petrol and air, it is shown that the igniting power of a spark increases with both the capacity discharging and the spark potential, but varies much more rapidly with the latter factor. The energy required for ignition decreases rapidly as the spark potential increases, and there is no indication that, if the spark potential were sufficiently increased, the energy required for ignition might not be reduced greatly beyond the measured limit, namely, 0·0004 joule. Other things

being equal, electrodes with small radius of curvature have greater igniting power; the metal of which the electrodes is made is of no importance from the point of view of ignition. J. F. S.

The State of Super-conductivity in Metals. C. A. Crommelin (*Chem. Weekblad*, 1919, **16**, 640—669).—A lecture delivered before the Natuurkundig Gezelschap in Leiden. Special reference is made to the work of Kamerlingh Onnes. W. S. M.

Electromotive Activity of Carbon Monoxide. II. K. A. Hofmann and B. Wurthmann (*Ber.*, 1919, **52**, [*B*], 1185—1194).—It has been previously shown (this vol., ii, 8) that the oxidation energy of carbon monoxide at the ordinary temperature can be largely converted into electrical energy when the carbon monoxide is oxidised at a copper electrode wetted with alkali hydroxide solution which is connected with a copper or platinum–air electrode. It is now shown that, in contrast to hydrogen, the activity of carbon monoxide is 0·12 volt greater at a copper than at a hydrogen electrode, and, further, that the potential developed by the oxidation of carbon monoxide is greater than that developed from hydrogen by 0·3 to 0·08 volt. A copper electrode is particularly useful in the utilisation of air in the carbon monoxide cell, since it forms a primary oxide with the oxygen the oxidative power of which is more than 0·2 volt greater than that of cupric oxide.

The potentials of the following cells are recorded, the electrolyte being 15% pure potassium hydroxide solution in every case: H_2|Pt, electrolyte, HgO|Hg, 0·93 volt at 22°; CO|Pt, electrolyte, HgO|Hg, 0·91 volt; CO|coppered carbon, electrolyte, HgO|Hg, 0·96 volt at 17—18°; CO|coppered carbon, electrolyte, Pb|air, 1·17 volt at 14°; CO|platinised carbon, electrolyte, Pt|air, 1·05 volt at 18°; CO|Cu, electrolyte, copper oxide|air, 0·95—0·99 volt at 20°; CO|platinised platinum, electrolyte, copper oxide|air, 0·91 volt at 18°; H_2|platinised platinum, electrolyte, copper oxide|air, 0·958 volt at 18·3°. H. W.

Methods of Measuring Electric Cataphoresis. The. Svedberg and Hugo Andersson (*Kolloid Zeitsch.*, 1919, **24**, 156—165).—The various methods which have been used for measuring the migration velocity of colloidal particles in an electric field are critically discussed and their errors enumerated. It is held that none of the methods hitherto described is entirely satisfactory, although that due to Linder and Picton (T., 1897, **71**, 568) is usable in some circumstances. The authors describe the construction of a small vessel in which microscopic cataphoresis experiments may be carried out with either direct or alternating current. A photomicrographic method is described by which cataphoresis may be measured by means of a direct current flowing for very short periods. A microscopic method is also described in which alternating current is used. A comparison of the results obtained by these methods shows that the latter is more exact and gives values

which more nearly agree with the theoretical values than the former. J. F. S.

Some Determinations of the Heat Conductivity of Selenium. Edna D. Sayce (*J. Proc. Roy. Soc. N.S. Wales*, 1917, **51**, 356—363).—It was found that the thermal conductivity of selenium varied over a wide range, and was affected by the conditions which influence its electrical conductivity, and in the same direction, but in general to a slighter extent. The thermal conductivity of vitreous selenium at 25° was found to lie between 0·000293 and 0·000328. That of crystalline selenium at 25° varied from 0·00070 to 0·00183. The values for the crystalline form increased in general with the temperature of preparation, but diminished with age. In all the cases examined, the temperature-coefficient was positive. All measurements were made with the selenium in darkness. W. G.

The Determination of the Melting Points of Fats and Similar Substances by Means of the "Ascension" Method. D. J. de Jong (*Pharm. Weekblad*, 1919, **56**, 925—931).—A short column of fat is allowed to solidify for twenty-four hours in a narrow glass tube open at both ends. The tube is placed vertically in water or glycerol so that the top of the fat column is below the level of the liquid. The temperature of the bath is raised slowly until the melting point is reached, at which temperature the column of fat begins to rise in the tube. Constant results were obtained when a thin-walled tube of 1 mm. internal diameter was used with a fat column 1 cm. long placed 1 cm. below the surface of the water. W. S. M.

The Freezing Point of Solutions with Special Reference to Solutions Containing Several Solutes. Charles Edward Fawsitt (T., 1919, **115**, 790—801).

Cryoscopy in Acetylene Tetrabromide. R. Lespieau (*Compt. rend.*, 1919, **169**, 31—32).—Using benzene, chloroform, carbon tetrachloride, and ethyl ether as solutes, the author finds that the cryoscopic constant of acetylene tetrabromide, m. p. 0—0·13°, is 217, and that it varies but little with the nature of the dissolved substance or the concentration providing that the solution remains dilute. W. G.

Variation of the Vapour Pressure with the Temperature. C. Emilio Carbonelli (*Gazzetta*, 1919, **49**, i, 151—153).—If θ denotes the absolute critical temperature of any liquid, π its critical pressure, and f its vapour pressure at a temperature T lying between absolute zero and the critical temperature, results in close agreement with the experimental data are given by the formula $\lg \pi/f = (\theta - T)/T \,.\, \lg h\theta/T$, h being a constant characteristic for each liquid. The values of $\lg h$ are: for carbon disulphide,

2·21503; chloroform, 2·58134; alcohol, 3·6765; water, 2·92714; ethyl ether, 2·80416; benzene, 2·64664; sulphur dioxide, 2·79064; cyanogen, 2·92481; and ammonia, 2·79. T. H. P.

Maximum Vapour Pressures of Benzene and *cyclo*Hexane at Moderate Temperatures and Calculation of their Principal Specific Heats. G. Déjardin (*Ann. Physique.*, 1919, [ix], **11**, 253—291).—A more detailed account of work already published (see this vol., ii, 95). W. G.

The Saturated Vapour Pressures and the Heats of Vaporisation of Propyl Acetate at Different Temperatures. E. Ariès (*Compt. rend.*, 1919, **168**, 1188—1192).—Using the formula previously given (compare A., 1918, ii, 352) for calculating the value of the function Γ, from these results the author has calculated the saturated vapour pressures and heats of vaporisation of propyl acetate at different temperatures, and finds that the calculated values are in close agreement with those observed by Young. W. G.

Volatility. Otto Ruff (*Ber.*, 1919, **52**, [*B*], 1223—1238).—A theoretical paper in which the boiling point of the substance under atmospheric pressure is treated as a measure of its volatility. A series of tables is given showing the b. p. of fluorides, chlorides, hydrides, nitrides, and oxides as far as these have been determined. A discussion is then entered on with regard to the part played by mass, atomic volume, number of atoms in the molecule, negative minimal loading of the atoms in the molecule, and molecular symmetry on volatility. For details, the original paper must be consulted. H. W.

Thermochemistry of Organic Fluorine Compounds. Frédéric Swarts (*J. Chim. Phys.*, 1919, **17**, 3—70).—Using a Langbein calorimetric bomb in which the silica-containing parts have been replaced by platinum, the author has determined the heat of combustion of a very large number of organic fluorine compounds. The results are recorded as (i) heat of combustion per gram, (ii) molecular heat of combustion (*a*) at constant pressure and (*b*) at constant volume. The heat of formation is also calculated in each case. The method of preparation, density, freezing point, and boiling point are recorded for every compound. By comparing the present results with those of Berthelot for other substances, the heat of substitution of one atom of fluorine for one atom of hydrogen is calculated. The substitution of the first atom of fluorine for hydrogen increases the heat of formation by about 17 cal., although the value fluctuates considerably for the various types of compounds; the introduction of the second atom of fluorine increases the heat of formation more than the first in all cases. The effect of substituting fluorine in benzene derivatives is also studied. It is shown that the replacement of one hydrogen

atom by fluorine increases the heat of formation by 15·8 cal., but the second further increases it by 22·3 cal. if the second atom enters the para-position. The substitution of fluorine in mono-substituted benzenes increases the heat of formation from 8·15 cal. in the case of *o*-fluoronitrobenzene to 22·6 cal. in the case of *m*-fluorophenol. Similar calculations are made for tri- and tetra-substitution products of benzene. J. F. S.

Heat of Coagulation. H. R. Kruyt and Jac. van der Spek (*Kolloid Zeitsch.*, 1919, **24**, 145—155).—The heat change occasioned by the sudden coagulation of arsenic sulphide sol and ferric oxide sol has been determined. In the case of arsenic sulphide, the coagulation was brought about by the addition of a solution of alum or potassium chloride. In all experiments, the heat change was extremely small, the amount of heat developed being 0·01—0·05 gram cal. per gram of arsenic sulphide. Ferric oxide sols were coagulated by the addition of sodium sulphate solution, and in this case the heat developed was considerably greater, amounting to 2 gram cal. per gram of ferric oxide. Experiments show that the heat developed depends very largely on the chlorine content of the sols. It is in keeping with expectation that there should be a considerable difference in the development of heat in the two cases, for the coagulation of ferric oxide sol is accompanied by a considerable increase in volume, whilst that of arsenic sulphide is accompanied by a very small diminution in volume. Further experiments were made to determine the heat change brought about by the adsorption of crystal-violet by animal charcoal. The results are only approximate and give the order of magnitude of the change; thus 5 grams of charcoal adsorb 2·21 millimols of crystal-violet with a heat absorption of 16·58 gram cals. For calculations of the amount of energy set free in the coagulation of arsenic sulphide sol, compare Linder and Picton (T., 1892, **61**, 114). J. F. S.

Calculation of the Divergences from Avogadro's Law by the Method of Compressibilities. Application to Hydrogen Bromide. Ph. A. Guye (*J. Chim. Phys.*, 1919, **17**, 141—170).—A theoretical paper in which it is shown that the work of Moles (A., 1916, ii, 42, 526) and Reiman (A., 1917, ii, 137, 200) on the density of hydrogen bromide definitely indicates that the compressibility (pv) of this gas at 0° and at pressures above 1 atm. is not a linear function of the pressure (p) nor of the inverse of the volume ($1/v$). This being the case, the product pv ought to be represented by a formula of the second degree of p or $1/v$, and this equation ought to hold for all gases less volatile than carbon dioxide. By means of the modified van der Waals's equation, it is known at once whether a gas ought to be represented in the neighbourhood of 1 atm. by an equation of the first or second degree. The use of a formula of the second degree, $(pv)=1+\alpha+ap+bp^2$, or $(pv)=1+\alpha^1+a^1/v+b^1/v^2$ for the extra-

polation of the limiting value $(pv)_0$ which enters into the expression, giving the divergences from Avogadro's law, is justified by consideration of the best established equations of state. Two methods are indicated for calculating the constants of the preceding equations, and when these are applied to the results of Moles and Reiman (*loc. cit.*), the following values are obtained for hydrogen bromide at 0°: (i) divergence from the law of Avogadro: $(1+\lambda)=(pv)_0/(pv)_1=1{\cdot}00934$; (ii) divergence of the compressibility between 0 and 1 atm.: $A^1{}_0=0{\cdot}00925$. The experiments of Moles and Reiman lead to the same results. The methods adopted in these calculations are discussed at some length in the paper.

J. F. S.

Investigation of Poisson's Ratio by Means of the Gaseous Volume and Specific Heat at Low Temperatures. Rudolf Mewes (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1918, **10**, 93; from *Chem. Zentr.*, 1919, i, 505).—A formula has previously been developed whereby the specific volumes of gases can be estimated from observation on the specific heats $k=c_p/c_v$ and c_p at low temperatures. The ratio v_{15}/v_t and v_0/v_t has been calculated from the formulæ $v_{15}/v_t=(1+\alpha)^{-t}$ and

$$v_{15}/v_t=v_{15}/[At(c_p-c_p/k)/P+v_{15}]$$

and introduced into Poisson's equation. Since the calculated and experimental results are not in harmony, Poisson's equation does not appear to hold good. H. W.

Gaseous Volumes at Low Temperatures. Rudolf Mewes (*Zeitsch. Sauerstoff Stickstoff Ind.*, 1918, **10**, 81—82; from *Chem. Zentr.*, 1919, i, 505).—Theoretical considerations based on a table which gives the necessary data for helium, hydrogen, nitrogen, oxygen, air free from carbon dioxide and carbon monoxide, show that Gay-Lussac's law is not approximately obeyed at low temperatures (at about −192°), and that the most accurate observations yet made are vitiated by some error which is not yet explained. H. W.

Modification of Victor Meyer's Vapour Density Apparatus. Giovanni Romeo (*Gazzetta*, 1919, **49**, i, 172—174).—In this apparatus, the upper, narrow, tubular part above the bulb in which the substance is vaporised is considerably shortened, and round it is wrapped, in the form of a spiral, the tube through which the displaced air passes to the graduated measuring tube. The lower end of this spiral tube is connected with the top of the bulb, whilst the upper end emerges through the stopper of the jacket containing the heating vapour. In this manner, the apparatus is made shorter and more easily manipulated, less time is required for the uniform heating of the apparatus, and condensation of the vaporised substance on the cool parts of the apparatus is entirely avoided. T. H. P.

The Adsorption of Helium by Charcoal. Stuart McLean (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 79—81).—A very

small amount of helium is adsorbed by charcoal at the temperature of liquid air, the amount adsorbed being apparently independent of the volume of helium introduced into the apparatus. W. G.

An Apparatus for Studying the Dissociation of Carbonate Rocks. G. A. Bole (*J. Amer. Ceram. Soc.*, 1919, **2**, 410—417). —The dissociation of carbonate rocks may be studied by heating 0·1 gram of the sample in a modification of Victor Meyer's vapour density apparatus, consisting of a small platinum bucket which fits over the lower end of the porcelain sheath of a thermocouple and is held in place by a small porcelain wedge. The thermocouple is then placed in a tube of fused silica, 25 cm. long and 1·25 cm. in diameter, provided with a side-tube leading to a pneumatic trough and gas burette. The top of the silica tube is closed with a ground-glass stopper, into which are fused the wires of the thermocouple. The stopper also contains a glass tube carrying a stopcock. The lower part of the silica tube is surrounded by an electric furnace. The temperature of the sample is raised to about 450°, with the stopcock open to expel any moisture. The stopcock is then closed, the temperature raised steadily, and the volume of gas evolved is measured at regular intervals of time until the dissociation is complete. The gas is examined for carbon monoxide, and, if this is found, a fresh portion of the sample is treated for removal of organic matter, and a fresh determination of the dissociation temperature is then made. It is necessary to make a blank test in order to ascertain the expansion of the air in the apparatus at various temperatures and to correct the volume of gas accordingly. The same apparatus may be used for determining the temperature at which the dissociation pressure is just above that of the atmosphere by maintaining it at the highest temperature at which gas is evolved. In determining the rate of dissociation, 0·5 gram of the sample is placed in a small platinum bucket in the neck of the apparatus, the silica tube is heated to about 50° above the temperature at which the determination is to be made, the temperature allowed to fall slowly to the desired temperature and maintained constant for about fifteen minutes. The bucket is then released and allowed to fall to the bottom of the tube, and the gas evolved is measured after a definite interval of time. A series of determinations is made at increasingly higher temperatures, and the results are plotted. The apparatus may also be used to determine the carbon dioxide associated with lime and magnesia respectively in limestone and dolomite by raising the temperature to 750° while the sample is in the neck of the tube, then releasing the bucket, raising the temperature to 900°, and measuring the gas evolved at each temperature. The apparatus is simple, easy to use, rapid, and accurate. Organic matter, occluded gases, and moisture may be driven off by manipulating the stopcock immediately before making a determination. A. B. S.

Piezo-chemical Studies. XV. Experimental Proof of Braun's Law. Ernest Cohen and A. L. Th. Moesveld (*Zeitsch. physikal. Chem.*, 1919, **93**, 385—515. Compare A., 1917, ii, 566). —With the object of ascertaining experimentally the extent to which Braun's law is true, the authors have determined (i) the temperature-coefficient of the solubility of *m*-dinitrobenzene in ethyl acetate, (ii) the pressure-coefficient of the solubility, (iii) the fictitious volume change, and (iv) the fictitious heat of solution of the same pair of substances (see A., 1918, ii, 297). These values when obtained were substituted in the expression

$$(dx/d\pi)_T : (dx/dT)_\pi = -T\Delta V/Q,$$

and the value of Q obtained and compared with the experimentally determined value of Q. In the expression above, $(dx/d\pi)_T$ is the pressure-coefficient of the solubility at constant temperature, $(dx/dT)_\pi$ the temperature-coefficient of the solubility at constant pressure, ΔV the fictitious volume change, that is, the volume change when a fixed amount of substance dissolves in an infinitely large volume of solvent at the temperature T, and Q the fictitious heat of solution. The value of Q found by this equation is 21·07±0·10 gram cal./gram, whereas the experimental value of Q is 21·02±0·02 gram cal./gram. From these figures, it is concluded the Braun law holds within the limits of experimental error. The solubility of *m*-dinitrobenzene in 100 grams of ethyl acetate is found to be 21·80 grams at 0·02°, 23·35 at 2·48°, 24·92 at 5·00°, 26·62 at 7·50°, 28·55 at 10·00°, 30·66 at 12·50°, 32·95 at 15·00°, 35·45 at 17·50°, 38·20 at 20·00°, 41·20 at 22·50°, 44·60 at 25·00°, 48·38 at 27·50°, 52·53 at 30·00°, 57·24 at 32·50°, and 62·32 at 35·00°. Calculating from these figures, the temperature-coefficient at 30·00° is found to be 0·5653±0·0007 gram mols. per 100 mols. of solution per degree, or 0·755?±0·001 gram per 100 grams of solution per degree. An apparatus is described whereby the solubility under various pressures may be determined. Using this apparatus, the solubility of *m*-dinitrobenzene in ethyl acetate is determined at 30° under pressures 0, 100, 220, 300, 380, and 480 atmospheres, and from the results the pressure-coefficient of the solubility calculated to $(dx/d\pi)_{\pi=1} = -0{\cdot}00867 \pm 0{\cdot}00003$ mol. %/per atm., or, if c=weight %, $(dc/d\pi)_{\pi=1} = -0{\cdot}01161 \pm 0{\cdot}00005$ weight %/per atm. The specific volume of various solutions of *m*-dinitrobenzene in ethyl acetate has been determined at temperatures between 20·00° and 30·00° by means of an Ostwald-Sprengel pyknometer, and also by a dilatometric method. From the results, it is shown that $v_c = 0{\cdot}96978$, that is, the specific volume of a solution saturated at 30·00° and 1 atm. pressure. The specific volume of solid *m*-dinitrobenzene at 30·00° was determined by a dilatometric method, using water as the liquid, and the value 0·63872 found. From the data thus accumulated, the fictitious volume change is calculated, and the values 0·0442 ± 0·0001 c.c./gram and 7·392±015 c.c./mol. obtained. A long description of the method of experimentally obtaining the fictitious heat of solution is given, and from the experiments the value 21·02±0·025 gram cal./per

gram, or 3534±5 gram cal./per mol., obtained. The paper ends with a long and detailed criticism of a paper on the same subject by H. F. Sill (A., 1917, ii, 75). J. F. S.

Liquid Crystals and Anisotropic Liquids. D. Vorländer (*Zeitsch. physikal. Chem.*, 1919, **93**, 516—520).—Polemical against Baur (*Jahrb. Chem.*, 1916, **25**, 362), Bose (A., 1907, ii, 443; 1908, ii, 1017), Nernst (*Lehrb. theoret. Chem.*), and Herz (*Moderne Probleme allgem. Chem.*). The author protests against the views put forward by the authors named, that liquid crystals are heterogeneous substances consisting of a disperse phase and a dispersion medium. J. F. S.

Orientation of Anisotropic Liquids on Contact with Crystals. II. F. Grandjean (*Bull. Soc. franç. Min.*, 1917, **40**, 69—105; from *Chem. Zentr.*, 1919, i, 498—499. Compare A., 1917, ii, 451).—The author describes the behaviour of the same crystals which were previously used with five new anisotropic liquids, *p*-azoxyanisolephenetole, dibenzylidenebenzidine, *p*-ditolylidenebenzidine, methoxycinnamic acid, and *p*-anisylideneaminoazotoluene. Orientation occurs in ninety cases out of a hundred, and hence is a general property. The crystal surface causes a peculiar field of force, the nature of which is not explained. It orientates anisotropic liquids in such a manner that their axes can assume one or more definite positions, which are termed equilibrium or field directions. One of these is perpendicular to the face of the crystal. If the latter corresponds with a net plane of high density, there is generally one or more of these directions parallel to the face. With respect to behaviour on change of temperature, three types are to be considered, in which (i) the orientation is not greatly altered, (ii) a well-defined orientation suddenly passes into a second arrangement, and (iii) the orientation changes gradually with changing temperature. H. W.

Periodic Precipitation. (Miss) A. W. Foster (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 55—57).—The addition of one drop of a 1% solution of silver nitrate to a thin sheet of gelatin impregnated with potassium chromate produced precipitation in the form of Leisegang's rings. When a colloidal copper solution was used instead of water for making the gelatin plate, the precipitate was not in the form of rings, but as microscopic quantities scattered over the plate. Similar experiments were performed, agar being used instead of gelatin, and it was found that in this case the presence of the positively charged copper particles did not change the character of the precipitate. W. G.

Rhythmic Solidification. D. Vorländer and Ilse Ernst (*Zeitsch. physikal. Chem.*, 1919, **93**, 521—526).—Solutions on evaporation in many cases deposit crystals in a rhythmic manner. This phenomenon is particularly well observed in the crystallisation of an aqueous solution of 5-nitrophenyl-2-glycine-1-carboxylic acid;

this substance crystallises in open vessels in a series of rings, the formation of which is connected with the surface tension and the adhesion of the solution on the vessel walls, and is also due to the fact that after the deposition of the first crystals the solution is drawn by capillary attraction to the crystals. As the evaporation proceeds, the surface tension of the solution overpowers the adhesion and capillary attraction, so that the solution withdraws itself spasmodically from the edges of the dish. In the case of molten substances, the authors have found very few substances which solidify rhythmically, but this phenomenon is well shown by the ethyl ester of *p*-ethoxybenzylideneaminophenylpropionic acid. This substance, which was prepared by the method described by Beilstein and Kuhlberg (*Annalen*, 1872, **163**, 162), melts at 59° to an amorphous liquid; on supercooling the molten substance to 34°, it forms liquid crystals. The rhythmic solidification occurs when either of the liquid forms passes into the crystalline solid, and takes place as follows: When a few drops of the molten substance are placed on a clean glass plate, a small, round, crystalline mass first forms; this exerts a capillary attraction on the surrounding liquid, and the liquid rises in the crystal mass and solidifies on top of it, and also on the sides, whilst the level of the liquid falls. Then a period of no growth of the crystal height sets in, because the adhesion of the liquid to the glass plate has overpowered the capillary attraction, but at the same time the crystal mass begins to grow rapidly from the sides until a quantity of liquid is held in the crystal network, when the side growth ceases and the vertical growth recommences. These three processes then repeat themselves in the same order. Photomicrographs illustrating the crystallisation in this case are appended to the paper. J. F. S.

New Method of Weighing Colloidal Particles. E. F. Burton (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 480—483).—A preliminary paper in which it is shown that by superimposing on a colloidal particle the motion produced by an electrical field on that produced by gravitation, colloidal solutions which possess particles too small to settle under the influence of gravity alone may be made to settle. The experimental procedure consists in superimposing on a colloidal solution contained in a migration tube a small column of conductivity water of the same specific conductivity as the colloidal solution. The position of the interface between the two liquids is noted, and a current of *E.M.F.* ca. 100 volts is passed for ten minutes, reversed, and again passed for ten minutes. The position of the interface is noted at the moment of reversal and at the end of the experiment. In the first period of ten minutes, the motion of the particles is due to a force $Xe+mg$ and in the second ten minutes to $Xe-mg$. From these values, the equation $a^2=9/2\,.\,nv/(\rho-\rho^1)g$ is deduced, in which a is the radius of the particle, v the velocity under the influence of gravitation, ρ and ρ^1 the densities of the particle and medium respectively, n the viscosity of the solution, and g the gravitational force. By

this method, colloidal particles of silver were found to have a radius $2{\cdot}2 \times 10^{-5}$ cm., whereas $1{\cdot}7 \times 10^{-5}$ was obtained by the counting method. The velocity v was $8{\cdot}3 \times 10^{-5}$ cm. per sec.

J. F. S.

Colours of Colloids. V. Metallic and Vitreous Lustre. Wilder D. Bancroft (*J. Physical Chem.*, 1919, **23**, 289—347).—A continuance of the discussion on colour phenomena dealt with in previous papers (A., 1918, ii, 102; this vol., ii, 187, 275). In the present paper, metallic and vitreous lustre as it affects colour is discussed in connexion with minerals, feathers, and beetles.

J. F. S.

Emulsification of Water and of Ammonium Chloride Solutions by Means of Lamp Black. William C. Moore (*J. Amer. Chem. Soc.*, 1919, **41**, 940—946).—Weighed quantities of lamp black, both the commercial article and that previously extracted with benzene, were stirred for measured times with petroleum (D^{15} 0·8149) and water or solutions of ammonium chloride of known concentration. The emulsions thus obtained, in which petroleum was the continuous phase, were examined under a micrometer microscope, and the diameter of the aqueous drops measured. The experiments show that various samples of lamp black have widely differing emulsifying properties. With a large quantity of lamp black, smaller emulsified drops of water are obtained in petroleum than when less lamp black is used. Water wets commercial lamp black less readily than the extracted lamp black. Ammonium chloride in normal solution wets the commercial lamp black more readily than the purified substance. Water wets purified lamp black more readily than does ammonium chloride solution, the converse being the case for the commercial lamp black. The drops of emulsified water become larger the greater the concentration of the ammonium chloride, owing to the increasing surface tension of the ammonium chloride solution. The effect of changing the time of stirring is somewhat indefinite; a tendency is shown for the size of the drops to pass through a minimum as the time is increased.

J. F. S.

Electromagnetic Hypothesis of the Kinetics of Heterogeneous Equilibrium, the Structure of Liquids and Cohesion. William D. Harkins and H. H. King (*J. Amer. Chem. Soc.*, 1919, **41**, 970—992).—A theoretical paper in which an hypothesis is developed that the distribution of a solute between various phases and interfaces is conditioned by the intermolecular electromagnetic fields. Cohesion is considered to be due to these fields, and is explained on the basis of the valency theory of Lewis (A., 1916, ii, 310) as being due to intermolecular fitting of electrons in the outer shells of atoms. The constant surface film of butyric acid on the surface of water is found to contain $2{\cdot}78 \times 10^{14}$ molecules, whilst if benzene covers the water phase, the layer contains

$2{\cdot}79 \times 10^{14}$ molecules per sq. cm. Thus the presence of benzene does not affect the number of molecules in the film. A theory of solubility and of thermodynamic environment is developed, and an hypothesis is made to explain the variation of the fugacity or thermodynamic potential of a component, with variations in its environment. In this connexion, solubility, Raoult's law, melting point, compressibility, coefficient of expansion, latent heat of vaporisation, adsorption, and surface structure are discussed. The theory is complicated, and the original should be consulted for details. J. F. S.

Chemical Affinity. Fritz Ephraim (*Naturwiss.*, 1919, **7**, 49—55; from *Chem. Zentr.*, 1919, i, 409—410).—The energy of a reaction is, in general, the sum of the energies of a number of component reactions, and therefore gives little information about the latter. The energy of analogous reactions is best studied with closely related compounds, whereby the common side-reactions are most readily eliminated. In this manner, the relative affinity of water of crystallisation to different molecules is conveniently determined by investigation of substances such as the alums. Studies of this nature are best effected by estimation of the affinities of subsidiary valencies with hydrates, and particularly ammines. The gaseous nature of ammonia allows the thermochemical investigation to be replaced by determination of the dissociation temperature, that is, the temperature at which the pressure of ammonia is equal to the atmospheric pressure. The affinity of ammonia for the molecule in question is obviously greater as the dissociation temperature is higher. The following compounds have been compared in this manner: $NiI_2,6NH_3$, $CoI_2,6NH_3$, $FeI_2,6NH_3$, $MnI_2,6NH_3$, $ZnI_2,6NH_3$, $CdI_2,6NH_3$. The temperature of decomposition decreases with increasing atomic volume, and the product of dissociation temperature and atomic volume is approximately constant. Consequently, the dissociation temperature can be calculated if that of a similar substance and the atomic volume of the metal are known, and, conversely, unknown atomic volumes can be calculated from the observed dissociation temperature. Irregularities are only observed with cadmium. When compounds of a metal with different acid radicles are investigated, the size of the latter appears to be important, but its effect can only be estimated with difficulty, since, in complex radicles, only that portion which is closely related to the metallic atom should be considered. The affinity for neutral molecules is particularly marked with large acid radicles. The relationships are most favourable when the metal is surrounded by acid radicles, as in the case of a multivalent metal united to several univalent radicles. With increase in volume of the neutral molecules, as with transition from ammonia to alkylamines, the affinity decreases. With complex cations, the neutral portion is more firmly bound as the size of the metal decreases. Conversely, the stability of complex ions increases with increasing volume of the metal. Systematic investigation of the

stability of a group of complex compounds permits the decision as to whether the complex is united to the anion or cation, and thus allows a determination of constitution in solid substances. The method is, in principle, applicable to all dissociable compounds. From this point of view, an explanation is given of the fact that the capacity of neutral salts to cause the separation of amino-acids is reversed by addition of traces of acid or alkali. The formation of dissociation equilibria is in many respects analogous to the evaporation of a liquid. The absolute boiling points under the same pressure of chemically related substances stand to one another in a constant ratio. The boiling-point rule can also be used as dissociation rule, as is shown in the case of the ammines of the iodides previously described. The rule is also true for substances of widely differing chemical nature. The calculation of the dissociation temperature for any pressure is therefore possible when it is known at any definite pressure. The limits of existence of compounds can therefore be defined. H. W.

Fission of Acid Salts in Aqueous Solution into Normal Salts and Free Acids. W. Dieckmann and Albin Hardt (*Ber.*, 1919, **52**, [*B*], 1134—1142. Compare Thoms and Sabalitschka, A., 1917, i, 700; Sabalitschka, this vol., ii, 282; McCoy, A., 1908, ii, 466; McCoy and Chandler, A., 1908, ii, 467).—It has been previously shown that dibasic organic acids can be partly extracted from aqueous solutions of their acid salts by treatment with ether, and McCoy has based a method of estimating the ratio of the first and second dissociation constants of such acids on this fact. The authors have repeated Chandler's work with camphoric and fumaric acids, and confirm his results. They have also applied the method to the determination of the second dissociation constant of homophthalic acid ($10^6k_1=191$), and obtained the value $k_1:k_2$ 212 (for $c=0{\cdot}001$), and therefore the value $10^6k_2=0{\cdot}9$. When contrasted with glutaric acid, which also contains the carboxyl groups in the 1:3-position ($10^6k_1=47{\cdot}4$, $k_1:k_2=14$, $10^6k_2=3{\cdot}38$), the ratio $k_1:k_2$ appears greatly increased, and here, as in other cases, to be subject to constitutive influences as well as to those due to the relative position of the carboxyl groups. Experiments with benzylmalonic acid and β-phenylglutaric acid show that the ratio of the constants, in comparison with those of the parent substances, is not greatly affected by the entry of a substituent in the symmetrical position. Comparison of δ-keto-β-phenyladipic acid,

$$CO_2H\cdot CH_2\cdot CHPh\cdot CH_2\cdot CO\cdot CO_2H$$

($10^6k_1=9300$, $k_1:k_2=850$, $10^6k_2=11$), with adipic acid ($10^6k_1=37{\cdot}6$, $k_1:k_2=15{\cdot}7$, $10^6k_2=2{\cdot}4$) shows a considerable increase in the first dissociation constant which can with certainty be ascribed to the presence of the carbonyl group; in addition, both the ratio $k_1:k_2$ and k_2 are increased, which is not in accordance with Smith's rule (A., 1918, ii, 155) that a substituent has an unlike influence on the two carboxyl groups.

The statement of Thoms and Sabalitschka (*loc. cit.*) that phthalic

acid can be extracted by ether from aqueous solutions of its normal sodium salt could not be confirmed, nor do the authors find that phthalic acid suffers partial dehydration when its ethereal solution is evaporated on the water-bath. H. W.

Chemical Processes in Solution and their Velocity. MAX TRAUTZ (*Zeitsch. anorg. Chem.*, 1919, **106**, 149—188).—A purely mathematical paper in which the theory of gas reactions (compare A., 1918, ii, 151) is discussed in relation to the quantum theory and is applied to reactions in solution. Owing to the nature of the paper, satisfactory abstraction is impossible, but it may be stated that it is found that the integration constant of the reaction velocity in solution is identical with that in gases. E. H. R.

The Law of Action of Sucrase: Influence of Viscosity on the Velocity of Hydrolysis. H. COLIN and (MLLE.) A. CHAUDUN (*Compt. rend.*, 1919, **168**, 1274—1276. Compare A., 1918, i, 414; ii, 357).—The authors show that the velocity of hydrolysis of sucrose, the amount of sucrase remaining constant, is directly proportional to the fluidity of the solution. The ratio dV/dF, for solutions of varying sucrase content, is proportional to the amount of sucrase present for a given sucrose concentration. W. G.

The Hydrolysis of Ethyl Acetate. L. BERCZELLER (*Oesterr. Chem. Zeit.*, 1919, **22**, 66—67).—The hydrolysis of ethyl acetate by hydriodic, hydrobromic, hydrochloric, and nitric acids has been studied with the object of determining the effect, if any, of the anion on the rate of the reaction. For each experiment, 10 c.c. of $N/2$-ethyl acetate solution were mixed with 1, 2·5, 5, 10, or 40 c.c. of $N/2$-acid solution and allowed to remain for times varying from a quarter of an hour to twenty-eight hours, at the end of which time the solution was titrated with $N/5$-potassium hydroxide. The rates of hydrolysis are not equal for the different acids, the strengths of the acids being in the order $HI>HBr>HCl>HNO_3$. It is thus shown that in this typical case of catalysis the effect is not confined to the hydrogen ion, the chemical nature of the anion having the same influence here as in the so-called neutral salt action. The presence of iodine in the hydriodic acid was found to have a retarding influence on the reaction. E. H. R.

Definition of the Terms: Explosion, Explosive Action, Thermite. A. LANGHAUS (*Zeitsch. ges. Schiess. u. Sprengstoffw.*, 1918, **13**, 310—313; from *Chem. Zentr.*, 1919, i, 692—693. Compare this vol., ii, 219).—The definitions given in the literature lay stress on the function of gaseous factors in explosive decomposition and scarcely mention the importance of chemical decomposition, to which the author attributes prime importance, since actual explosions and explosive actions can be distinguished by it. The

following definitions only take into account the nature of the reaction; a definition in the strict physicochemical sense will be given later.

True explosion is the chemical decomposition of a substance in a definite manner which is distinguished by development of heat (chemical importance), sound (physical importance), and destruction of the immediate surroundings in consequence of high velocity of decomposition (technical importance). In decomposition of this kind, gases, either pre-formed or generated, are the chief agents. (1) *Direct Gas Explosions.*—The pre-formed gases are the actual carriers of the explosion, whilst the gaseous products cause the external physical and technical effects; the explosion may be total, as with oxyhydrogen gas, or partial, as with gas and solid or liquid substance, as in the cases of dust explosions, ether, and petroleum explosions. (2) *Indirect Gas Explosions.*—The gases do not react chemically and are not the carriers of the actual explosion, but merely cause the physical and technical effects. Two cases are to be distinguished, in the first of which a gas is present in which the solid or liquid substance explodes (silver acetylide, aluminium, or magnesium with an oxygen carrier, potassium chlorate and antimony sulphide, percussion gases), whilst in the second class the gas is generated by decomposition of solid or liquid substances (true explosives, such as nitroglycerol, gunpowder, picric acid). The substances capable of such decomposition are termed explosive substances.

Explosion-like actions are such as show external characteristics similar to those outlined above, but do not involve chemical action. With gaseous substances, gas may be pre-formed (lightning in air, explosion of bombs filled with compressed gas) or may be generated (boiler explosions, quicklime and water in a closed vessel); with liquids, such action is observed in the case of vessels filled with liquid, and examples with solids are afforded by Rupert's drops and explosive antimony. H. W.

Emission Spectra and Atomic Structure. John William Nicholson (T., 1919, **115**, 855—864).—A lecture delivered before the Chemical Society on March 6th, 1919.

The Quantum Theory and New Theories of Atomic Structure. James Hopwood Jeans (T., 1919, **115**, 865—871).—A lecture delivered before the Chemical Society on May 1st, 1919.

Arrangement of Electrons in Atoms and Molecules. Irving Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 868—934).—A theoretical paper in which a theory of the arrangement of electrons in atoms and molecules is put forward; this theory is essentially an extension of Lewis's theory of the cubical atom (A., 1916, ii, 310). The electrons in atoms are either stationary or rotate, revolve or oscillate, about definite positions in the atom.

In the most stable atoms, namely, those of the inert gases, the electrons have positions symmetrical with respect to a plane (equatorial plane) passing through the centre of the nucleus of the atom. No electrons lie in the equatorial plane. There is an axis of symmetry (polar axis) at right angles to this plane through which four secondary planes of symmetry pass, forming angles of 45° with each other. These atoms have the symmetry of a tetragonal crystal. The electrons of any atom are distributed through a series of concentric, nearly spherical shells, all of equal thickness. The mean radii of the shells are in the ratio $1:2:3:4$, and the effective areas are in the ratio $1^2:2^2:3^2:4^2$. Each shell is divided into cellular spaces or cells occupying equal areas and symmetrically distributed over the surface of the shell. The first shell contains 2 cells, the second 8, the third 18, and the fourth 32. Each cell in the first shell can contain only one electron, but every other cell can contain either one or two electrons. The inner cells must have their full quota of electrons before the outside shell can contain any. No cell in the outside shell can contain two electrons until all other cells in this layer contain at least one. The electrons in the same cell neither repel nor attract one another, which implies a magnetic attraction that overcomes the electrostatic repulsion. When the number of electrons in the outside layer is small, the arrangement of the electrons is determined by the magnetic attraction of the underlying electrons, but when the number of electrons increases, especially when the layer is nearly complete, the electrostatic repulsion to the underlying electrons and of those in the outside shell becomes predominant. The properties of the atom are determined primarily by the number and arrangement of electrons in the outside shell and by the ease with which the atom is able to revert to more stable forms by giving up or taking up electrons. The stable and symmetrical arrangements of electrons corresponding with the inert gases are characterised by strong internal and weak external fields of force. The smaller the atomic number, the weaker the external field. The most stable arrangement of electrons is that of the pair in the helium atom. A stable pair may also be held by (*a*) a single hydrogen nucleus; (*b*) two hydrogen nuclei; (*c*) a hydrogen nucleus and the kernel of a second atom; (*d*) very rarely by two atomic kernels. The next most stable arrangement of electrons is the octet, that is, a group of eight electrons like that in the second shell of the neon atom. Any atom with atomic number less than 20, which has more than three electrons in its outside layer, tends to take up enough electrons to complete its octet. Two octets may hold one, two, or three pairs of electrons in common. One octet may share one, two, three, or four pairs of its electrons with one, two, three, or four other octets. One or more pairs of electrons in an octet may be shared by the corresponding number of hydrogen nuclei. No electron can be shared by more than two octets. This theory explains the periodic properties of all the elements, including those of the eighth group and the rare earths.

It accounts for the magnetic and physical properties as well as the chemical properties. It leads to a simple theory of valency for both polar and non-polar substances. It explains the structure of compounds, which, according to Werner's theory, are second-order compounds with a co-ordination number equal to four. According to the present theory, such compounds are to be regarded as typical primary valency compounds. This valency theory is based on the equation $e=8n-2p$, where e is the total number of available electrons in the shells of all the atoms in a molecule, n the number of octets forming the outside shells, and p the number of pairs of electrons held in common by the octets. The theory leads to definite conceptions of the positions of the electrons in the molecules or space lattices of compounds. The structures of the molecules of nitrogen, carbon monoxide, hydrogen cyanide, and nitric oxide are exceptional, because the kernels of both atoms are contained within a single octet. This accounts for the practically identical physical properties of nitrogen and carbon monoxide and for the abnormal inertness of nitrogen. J. F. S.

The Derivation of the Periodic System of the Chemical Elements from the Electron Theory. Heinrich Teudt (*Zeitsch. anorg. Chem.*, 1919, **106**, 189—208).—Starting with the conception of the atom as a positively charged nucleus surrounded by rotating negative electrons, the author shows how many of the important properties of the periodic system of the elements follow from this conception. Two kinds of electrons are distinguished, an inner sphere firmly held by the attractive force of the positive nucleus and an outer sphere of valence electrons, through which combination with other atoms takes place. The rotating electrons are probably distributed symmetrically on spherical surfaces as near the equatorial zone of the atom as possible. Hydrogen is the only element which has only valence electrons, since its one electron functions in this manner. The two electrons of helium are both bound in the inner sphere, the element having no valence electrons, and the same is true of the other inert gases. The remaining elements have electrons of both kinds. Those of the first horizontal series have two electrons in the inner sphere, whilst the number of possible valence electrons increases from lithium (1) to fluorine (7). Some of the valence electrons tend to be retained in the inner sphere, however, for instance, when carbon becomes bivalent, nitrogen tervalent, oxygen bivalent, and fluorine univalent. In the second horizontal series, the inner sphere contains at least ten electrons, in the third series eighteen, and so on.

The metals are distinguished from the metalloids by their more mobile or less firmly held valence electrons. Passing from left to right in a horizontal series, the number of positive charges on the nucleus steadily increases, whilst the number of inner electrons remains constant, and in order to retain their position the latter must increase their centrifugal force by increasing their rotation velocity. At the same time, the valence electrons must increase

their rotation velocity to a corresponding degree to prevent disruption of the atom, and the whole electron system becomes more stable. It follows that the metalloid character of the elements increases from left to right of a horizontal series. In the third, fifth, and seventh horizontal series, however, the metallic character is maintained throughout. To explain this irregularity, it is supposed that in these series the inner sphere is made up of an odd number of rings of electrons, the central ring occupying the equatorial position. This central ring of electrons intercepts lines of force which, in the case of the second, fourth, and sixth series with even numbers of rings of electrons in the inner sphere, would serve to hold the valence electrons with greater force. It follows that the outer electrons of odd series are more mobile than those of the even series, and the elements of the former are therefore more metallic. The appearance of the iron, ruthenium, and osmium triads is attributed to the relative instability of the electron systems developed at the end of the third, fifth, and seventh horizontal series. The elements copper, silver, and gold are closely related to the respective triads which they follow, and should not be placed in Group I. As the number of electrons in the atom increases, the forces retaining the valence electrons become weaker, and consequently the metallic character of the elements becomes more marked with increasing atomic weight. The periodic progression of the atomic volumes of the elements is discussed in terms of the electron theory. E. H. R.

A New Periodic Classification of the Chemical Elements. Marc Chauvierre (*Bull. Soc. chim.*, 1919, [iv], **25**, 297—305).—Marking off the atomic weights as abscissæ and the principal valencies of the elements (from zero to four) as ordinates, a periodic curve the period of which is double is obtained, the elements of the iron, palladium, didymium, and platinum families, the atomic weights of which are close together, being placed above the level of quadrivalency. The elements which occur in the same periodic position on the curve have generally similar chemical properties and correspond with the natural groups of elements. The elements may also be arranged by this method in a table similar to that of Mendeléev. W. G.

Annual Report of the International Committee on Atomic Weights (T., 1919, **115**, 879—885).

The Alchemists Known as Hollandus. Edmund O. von Lippmann (*Chem. Zeit.*, 1919, **43**, 265—267, 286—288, 301—303).—In a long contribution to the discussion on the authenticity and period of Jan Isaac and Isaac of Holland, the author maintains his original view (A., 1916, ii, 525) against the criticism of Schelenz (A., 1917, ii, 529). E. H. R.

Basil Valentine. B. Neumann (*Zeitsch. angew. Chem.*, 1919, **32**, I, 184).—Polemical. A reply to Hommel (this vol., ii, 224). S. S. A.

Trustworthiness of the Balance over Long Periods of Time. George Dean (T., 1919, **115**, 826—828).

Laboratory Condensers for Use in Reflux Condensation and Distillation Apparatus. O. Faust (*Zeitsch. angew. Chem.*, 1919, **32**, I, 183—184).—A description is given of condensers, especially suitable for use as reflux condensers, which are provided at the same end with inlet and outlet tubes, one of which passes inside the jacket to the other end of the condenser, whereby counter-current cooling is obtained. The jacket is provided with an air outlet tap. Of the various designs illustrated, one is suitable for connexion in the usual way, another for suspension in the neck of the flask without cork connexion, and a third for fitting bodily into the neck of the distillation vessel. S. S. A.

Simple Efficient Vacuum Pump for Laboratory Use. Alfred Magnus (*Ber.*, 1919, **52**, [*B*], 1194).—A claim for scientific priority against Volmer (this vol., ii, 225). The application of a current of mercury vapour to the production of high vacua has been utilised by the author (*Inaug. Diss.*, München, 1905). H. W.

Lecture Experiments [to Illustrate] the Reduction of Hydrogen-ion Concentration. L. Grünhut (*Zeitsch. Elektrochem.*, 1919, **25**, 184—185).—Two experiments are described by which the reduction of the hydrogen-ion concentration may be demonstrated.

(1) By removal of hydrogen ions: 10 c.c. of 0·1*N*-hydrochloric acid are placed in each of two 100 c.c. cylinders, and a few drops of a solution of dimethylaminoazobenzene solution added. One cylinder is filled to the mark with distilled water and the other with a 0·1*N*-solution of disodium hydrogen citrate. The water solution is red in colour, whilst the other solution becomes yellow. The aqueous solution contains 9·7 mg.-ion per litre (P_H. = 2·013), whilst the citrate solution contains 0·015 mg.-ion per litre (P_H. = 4·83), that is, the hydrogen-ion concentration has been reduced to 1/650 of its original value. The colour change of dimethylaminoazobenzene occurs between P_H. = 3 and P_H. = 4.

(2) By repressing the ionisation: 100 c.c. of tartaric acid (40 grams per litre) are placed in each of two 100 c.c. cylinders and coloured blue by the addition of a few drops of methyl-violet solution. To one cylinder, 4 grams of finely powdered sodium tartrate are added; this, when dissolved, will change the colour to violet. The water solution contains 17·00 mg. $H^{\cdot}$ ion per litre (P_H. = 1·77), whilst the tartrate solution contains 0·96 mg. $H^{\cdot}$ ion per litre (P_H. = 3·02). The neutral point of methyl-violet lies between P_H. = 2 and P_H. = 3. J. F. S.

Inorganic Chemistry.

Physico-chemical Revision of the Atomic Weight of Bromine: Necessity of Correcting the Atomic Weight of Silver. Ph. A. Guye (*J. Chim. Phys.*, 1919, **17**, 171—186).—From the experiments of Moles (A., 1916, ii, 42, 526) and Reiman (A., 1917, ii, 137, 200), the weight of the normal litre of hydrogen bromide has been calculated to the value 3·64423 grams. The weight of a litre of hydrogen bromide at 0° and under a pressure of 2/3 or 1/3 atm. is given by 2·42197 grams and 1·20729 grams respectively. The divergences from Avogadro's law $(1+\lambda)$ and from the compressibility (A'_0) have been found to be $(1+\lambda)=1{\cdot}00934$ and $A'_0=0{\cdot}00925$ (see this vol., ii, 318). From these values, the atomic weight of bromine is calculated to 79·920. This value is slightly greater than the value obtained from the ratio Ag:Br, consequently it is suggested that the atomic weight of silver ought to be reduced to 107·87. J. F. S.

Recovery of Iodine from its Residues. F. Arndt (*Ber.*, 1919, **52**, [*B*], 1131—1134).—The residues are placed in a large flask provided with a rubber stopper which carries a tube reaching nearly to the bottom of the liquid. The other end of the tube is connected with a reversed wash-bottle and a source of oxygen. The residues (which should not more than half fill the flask) are acidified with crude sulphuric acid, and oxygen is passed into the flask. A small quantity of nitrite solution is added, the flask is securely corked, and passage of the oxygen is continued into the well-shaken liquid. Completion of the action is indicated by cessation of the oxygen absorption, when a further small quantity of nitrite should be added to make certain that all the iodine has separated. The crude iodine is purified by distillation with steam, the vapours being passed directly into a large Erlenmeyer flask, which is cooled by water and is also provided with a long, upright tube to serve as air condenser. The iodine which is thus obtained retains water with considerable obstinacy, and is most easily dried by warming it on the water-bath in a porcelain dish covered by a clock-glass; the latter is frequently removed and the deposit of moisture and iodine is scraped off. As soon as the sublimate appears perfectly dry, the main portion may safely be regarded as dry also. The iodine so obtained is pure.

If the original solution is free from organic matter of high molecular weight, such as starch, the distillation with steam may be omitted. H. W.

Electrolytic Production of Fluorine. W. L. Argo, F. C. Mathers, B. Humiston, and C. O. Anderson (*J. Physical Chem.*, 1919, **23**, 348—355).—The authors have prepared fluorine by the

electrolysis of molten potassium hydrogen fluoride. The electrolysis is effected in an electrically heated copper vessel which serves as cathode; the anode is made of graphite. The anode is enclosed in a permeable diaphragm, which prevents the hydrogen liberated at the cathode mixing with the fluorine. As the electrolysis proceeds, potassium fluoride and copper fluoride are deposited from the fusion, and after a while it becomes necessary to regenerate the electrolyte. The most efficient conditions for work are a temperature of 240—250° and a current of 10 amperes at 15 volts. Using these conditions, the current efficiency is about 70%. In the preparation, the potassium acid fluoride must be absolutely dry, and since this is difficult to obtain and keep on account of the hygroscopic properties of the salt, the authors prefer the corresponding sodium salt, which has the advantages: (i) it is non-deliquescent, (ii) it decomposes below the fusion temperature, (iii) it contains a larger quantity of available hydrofluoric acid, and (iv) it is considerably less expensive. The properties of fluorine which may be used for its detection are: (i) its not unpleasant odour (fluorine in small quantities is non-toxic, but long exposure to larger quantities produces headache); (ii) the unlighted gas issuing from a Bunsen burner is immediately ignited by fluorine; (iii) sulphur and soft charcoal are quickly ignited when the gas comes into contact with them. J. F. S.

Constitution of Sulphur Vapour. James J. Dobbie and J. J. Fox (*Proc. Roy. Soc.*, 1919, [*A*], **95**, 484—492).—The absorption spectrum of sulphur vapour has been photographed at the temperatures 380—1080°. Sulphur vapour was produced in a silica tube 100 mm. long and 12 mm. diam., and the measurements were made with a large Hilger spectrograph. Illumination was produced by a Nernst lamp for the visible region and the ultraviolet down to λ 3100, and for the region beyond the range of the Nernst lamp a cadmium arc was employed. Weighed quantities of sulphur were vaporised in the tube, which had previously been sealed at a pressure of 8 mm., the gaseous content being nitrogen; a further series of experiments was made at atmospheric pressure. The spectrum shortens as the temperature is raised to 650°, after which it lengthens again. The maximum absorption therefore occurs at this point. The authors find on extrapolating the vapour density results of Biltz (A., 1888, 1027) that at the temperature 650° the density corresponds with a molecule S_2. The authors are therefore of the opinion that at suitable temperatures sulphur vapour contains the molecules S_2, S_3, and S_8. J. F. S.

The Reduction of Sulphurous Acid by Hydrogen Sulphide in Aqueous Solution. Ernst Heinze (*J. pr. Chem.*, 1919, [ii], **99**, 109—178).—For the quantitative investigation of the reaction between sulphur dioxide and hydrogen sulphide in aqueous solution at different temperatures, an apparatus was constructed by means of which accurately measured quantities of the

gases could be brought successively into the reaction flask, in which water was already present, with complete exclusion of air. The course of the reaction was found to be very complicated and to involve a number of reversible reactions. It depends both on the relative proportions of the reacting gases used and on the order of addition. A considerable part of the paper is devoted to a description of the special methods devised for the analysis of the reaction liquor. It was found that the sulphur formed in the reaction could be obtained in a readily filterable form if a small quantity of lanthanum chloride was present in the solution. Any remaining hydrogen sulphide was estimated by precipitation with cadmium sulphate; sulphur dioxide was removed by a current of nitrogen, collected in sodium hydroxide solution, and estimated iodometrically, whilst polythionic acids were determined by titrating the remaining solution with barium hydroxide.

It is established, first, that sulphur dioxide enters into the reaction in the form of sulphurous acid, not in the anhydride form. The primary reaction appears to be represented by the reversible equation $H_2SO_3 + H_2S \rightleftharpoons H_2SO_2 + H_2SO$. Precipitation of sulphur is caused by the decomposition of the compound H_2SO, which is assumed to be of the hydrogen peroxide type. This compound is also supposed to be formed by the further action of hydrogen sulphide on the sulphoxylic acid, thus: $H_2SO_2 + H_2S \rightleftharpoons 2H_2SO$. Consequently, the final result of the interaction of one mol. of sulphurous acid with two mols. of hydrogen sulphide is given by the equation $2H_2S + SO_2 = 3S + 2H_2O$. The reaction only comes to completion, however, after several months. The final state is reached more quickly in presence of excess of hydrogen sulphide. It is shown experimentally that hydrogen sulphide also reacts with polythionic acids to form sulphur and water.

When excess of sulphurous acid is present, less sulphur is precipitated and more polythionic acid formed. After about a day, a condition of equilibrium obtains. If, now, the precipitated sulphur is filtered off and the excess of sulphur dioxide removed by a current of nitrogen, in a short time more sulphur comes down and sulphur dioxide again appears in the solution. It is shown that the sulphur, when once precipitated, takes no further part in the process, and the reversible reactions are supposed to involve the polythionic acids, sulphurous acid, and the compounds H_2SO_2 and H_2SO, thus: (4) $H_2SO_3 + SO_2 \rightleftharpoons H_2S_2O_4$;

(5) $H_2SO + H_2SO_3 \rightleftharpoons H_2S_2O_3 + H_2O$;

(6) $H_2S_2O_4 + H_2S_2O_3 \rightleftharpoons H_2S_4O_6 + H_2O$; (7) $H_2S_4O_6 + H_2S_2O_3 \rightleftharpoons H_2S_5O_6 + H_2SO_3$. With increasing concentration of sulphur dioxide, the proportion of tetrathionic acid increases, whilst that of pentathionic acid decreases. This is attributed to the dehydration of the sulphurous acid owing to the increasing acidity of the solution, with consequent increase in the production of $H_2S_2O_4$ by equation (4).

When solutions containing excess of sulphur dioxide are allowed to remain for several weeks, increasing quantities of sulphuric acid

are formed, but the mechanism of this change cannot at present be explained. Possibly it is due to the decomposition of trithionic acid, which may be formed in small quantities and is known to decompose into sulphuric acid, sulphur dioxide, and free sulphur.

E. H. R.

Action of Sodium Thiosulphate on the Hypochlorites. F. Diénert and F. Wandenbulcke (*Compt. rend.*, 1919, **169**, 29—30).—A quantitative study of the interaction of sodium thiosulphate and sodium hypochlorite in dilute solutions shows that the reaction proceeds according to the equation $3Na_2S_2O_3+5Cl_2+5H_2O=Na_2SO_4+8HCl+H_2SO_4+Na_2S_4O_6+2NaCl$ or $5NaOCl+3Na_2S_2O_3+5H_2O=2Na_2SO_4+Na_2S_4O_6+5NaCl+5H_2O$. In the presence of acids, however, or even in the presence of sodium hydrogen carbonate, much less sodium thiosulphate is required, the reaction being $Na_2S_2O_3+4Cl_2+5H_2O=2NaHSO_4+8HCl$.

W. G.

Selenic Acid and Copper Selenate. L. M. Dennis and J. P. Koller (*J. Amer. Chem. Soc.*, 1919, **41**, 949—970).—Selenium has been obtained from smelter flue-dust by fusing a mixture of 300 grams of flue-dust, 200 grams of anhydrous sodium carbonate, and 775 grams of sodium peroxide in a large nickel crucible until the mass melted quietly. After cooling, the product was treated with water and insoluble material filtered off; it was then nearly neutralised with hydrochloric acid, which precipitated most of the zinc and aluminium. After filtration, a large volume of hydrochloric acid was added, and the solution boiled for thirty minutes to reduce selenic acid to selenious acid; any silica present was precipitated at this stage; the filtrate was then heated to 80° and treated with sodium sulphite in small quantities. The selenium separates, and is converted into the grey modification by digesting it with the solution for several hours at 80°.

Anode slimes containing 96% of selenium were also used to prepare the pure element. The slime was added to concentrated nitric acid to which one-fifth of its volume of water had been added; a vigorous action ensued, and when this had moderated, the mixture was heated to complete the oxidation. The solution was filtered, and a viscous, dark green liquid obtained which was evaporated to dryness. The residue was taken up with hydrochloric acid (3:1) and the selenium precipitated by sulphur dioxide or sodium sulphite.

Pure selenium dioxide is prepared from selenium by dissolving the substance obtained above in nitric acid and evaporating the solution to dryness. The crude dioxide thus obtained was placed in one end of a glass tube 85 cm. long and 3·5 cm. diameter. The tube was covered with asbestos paper and placed in a 60 cm. combustion furnace; a 2 cm. thick plug of glass wool was placed in the middle of the tube. The tube was so arranged in the furnace that

only a small length protruded at the cold end. On heating the crude dioxide, it sublimed and condensed on the protruding part of the tube, and as this became full, more of the tube was pushed out of the furnace.

Selenious acid was prepared directly from anode slimes by oxidising with nitric acid and evaporating until a syrupy solution was obtained. On cooling, large crystals separated, and after four recrystallisations from water, pure selenious acid, quite free from tellurium, was obtained.

Tellurium may be detected in the presence of selenium by dissolving 10—20 grams of the oxide in hydrochloric acid (D 1·16), heating to 90°, and saturating with sulphur dioxide. The precipitated selenium is filtered off and the filtrate diluted with an equal volume of water and saturated cold with sulphur dioxide. An immediate black precipitate of tellurium is formed if this element is present. A yield of 1200 grams of selenious acid was obtained from 3000 grams of slimes.

Pure selenic acid has been prepared (i) by the oxidation of silver selenite by means of bromine, (ii) by the oxidation of copper selenite by chlorine, and (iii) by the electrolytic oxidation of selenious acid. In the last-named method, the most efficient yield is obtained when lead dioxide anodes, in thimbles, are used.

Selenious acid may be detected in the presence of selenic acid on the basis of the reaction $H_2SeO_3 + 4HI = Se + 4I + 3H_2O$. Concentrated selenic acid will also oxidise hydriodic acid, but if the solution is dilute, selenic acid will remain unchanged. If, therefore, small quantities of potassium iodide are added to solutions containing both selenious and selenic acid in test-tubes 15 cm. long, there will be a yellow colour produced, due to iodine being liberated, and when the colour of the iodine is discharged by the addition of a drop or two of sodium sulphite, the red turbidity due to free selenium is visible. If the selenic acid is more concentrated than 0·8%, iodine may be liberated by it, but as the hydriodic acid is not concentrated, the reaction goes no further. This reaction is capable of detecting 1 part of selenium dioxide in 18,400 parts of selenic acid, or 1 part of selenium dioxide in 2,500,000 parts of solution.

Sulphuric acid in the presence of selenic acid may be detected in the following manner. Selenic acid is diluted to 4%, placed in a 350 c.c. beaker, 10 c.c. of 90% hydrazine hydrate added, and heated to 60°. Sufficient concentrated hydrochloric acid (5 c.c.) is added to make the liquid distinctly acid, and the mixture boiled for an hour. After cooling, the precipitated selenium is filtered off, and the process repeated until no more selenium is deposited. The filtrate is then evaporated to 25 c.c., and 2 c.c. of 10% barium chloride solution are added, and the mixture kept at 80° for an hour, when a white turbidity is produced if sulphuric acid is present. This reaction is visible if 1 mg. of barium sulphate is formed, and it is possible to detect 1 part of sulphuric acid in the presence of 10,000 parts of selenic acid.

All attempts to prepare perselenic acid and perselenates by electrolysis gave negative results.

The monohydrate of copper selenate is produced from the pentahydrate by heating the latter at 102° for two hours. The pentahydrate is completely dehydrated at 230—235°, and the anhydrous selenate is stable up to 280°. The pentahydrate used in these experiments was prepared by the action of chlorine on copper selenite, and contained copper chloride; this was removed by extracting with acetone in a Soxhlet extractor. In this process, the pentahydrate lost $2H_2O$ and the trihydrate was formed; this substance has a pale blue colour.

Ammonia derivatives of copper selenate have been prepared by methods analogous to those used by Horn and Taylor (A., 1904, ii, 662) in the preparation of the corresponding derivatives of copper sulphate. (i) *Copper selenate tetra-ammoniate monohydrate*, $CuSeO_4,4NH_3,H_2O$, is prepared by digesting 100 grams of copper selenate pentahydrate with 125 c.c. of ammonium hydroxide (0·96) until it has dissolved; ammonia gas is then led in, and in a short time clusters of deep bluish-violet crystals separate. The crystals were dried by suction and finally air-dried. It is quite stable when kept over lime, but loses ammonia in the air; it crystallises in slender, orthorhombic prisms. (ii) *Copper selenate triammoniate monohydrate*, $CuSeO_4,3NH_3,H_2O$, is prepared by exposing the last described compound to a current of air for about twenty-four hours. It is a blue compound which dissolves in water to give a blue solution; this on dilution becomes lighter in colour and deposits a basic salt. (iii) *Copper selenate tetra-ammoniate*, $CuSeO_4,4NH_3$, is prepared from the first-named compound by placing it moist in a desiccator over lime at 25 mm. pressure and keeping it there for seven days. It is of a lighter bluish-violet colour than the hydrated salt; it gives off ammonia when exposed to the air, but is stable in a vacuum over lime.

J. F. S.

Formation of Ammonia by Means of an Electric Arc: Influence of Diminishing the Pressure. E. Briner and A. Baerfuss (*J. Chim. Phys.*, 1919, **17**, 71—140. Compare this vol., ii, 148).—The synthesis of ammonia from a mixture of nitrogen and hydrogen at reduced pressures by means of an alternating arc between electrodes of various metals has been studied under a long series of widely varying experimental conditions. It is shown that at sufficiently low pressures (150 mm. and below) the arc assumes the appearance of a luminous sheath, which surrounds the electrodes and becomes longer the lower the pressure and the larger the current. This sheath plays an important part in the synthesis of ammonia. On reducing the pressure, it is noted that successive decreases in the voltage of the arc have nearly the same effect in the two pure gases and their mixtures. At pressures of the order 600—700 mm., an increase in the arc current leads to an increase in the energy yield (*Rdt*), which is due to a lowering of the

voltage. Working at pressures of the order 100 mm. with the theoretical mixture of gases, there is an improvement in the value of Rdt which is to be attributed, for the most part, to the lowering of the voltage. At this pressure and with platinum electrodes, an increase in the nitrogen percentage leads to an increased quantity yield (Q) of about 200% for the optimum mixture of five volumes of nitrogen to one volume of hydrogen. Using different metals as electrodes, it is found that the metals of the platinum group give the best results, platinum itself being most efficient; these metals are followed in efficiency by tungsten and copper. Iron and nickel are very much less effective than the other metals mentioned, and for these the optimum yield is obtained from the theoretical mixture at all pressures. The presence of moisture does not appear to affect the synthesis; the presence of oxygen in small quantities in certain circumstances acts favourably on the reaction. At reduced pressures, the influence of the arc current appears to be connected with the temperature produced at the electrodes; for every electrode there is an optimum diameter for every current. For currents up to 0·020 amp., cooling of the region containing the arc does not increase the yield. At low pressures, the yields are almost independent of the distance between the electrodes, consequently it is advisable to reduce this space as much as possible, since it only plays a secondary part in the reaction. There is no appreciable formation of ammonia when nitrogen and hydrogen, which have been submitted to the arc, are allowed to mix. The foregoing results confirm in the main the theory of the formation of ammonia put forward by the authors. This theory states that ammonia is formed by the action of a high temperature followed by a kinetic phenomenon in the colder regions where the ammonia is stable in the concentration produced, rather than by the establishment of an equilibrium in the very cold regions. In the relatively cold regions, which are near the luminous sheath, the formation occurs between the elements which have previously been rendered active by contact with the electrodes. The activation of the elements appears to consist of the dissociation of the molecules into atoms at the very high temperature of the arc, and is favoured by a diminution of the pressure. Active nitrogen, described by Strutt, does not appear to take any part in the synthesis, and at the pressures employed does not appear to be formed. J. F. S.

Relations between Nitrogen Peroxide and Nitric Acid. P. Pascal and Garnier (*Bull. Soc. chim.*, 1919, [iv], **25**, 309—321). —Results obtained for the density of nitrogen peroxide over the temperature range 0—21·5° are in agreement with those of Cundall (compare T., 1891, **59**, 1076), being represented by the equation $D_4' = 1·490 - 0·00215t$. The density of nitrogen peroxide is lowered by the addition of nitrous anhydride, the variations of density with the composition of the mixture obeying a linear law.

The density of nitric acid shows a marked increase with the addition of nitrogen peroxide (compare Lunge and Marchlewsky,

Zeitsch. angew. Chem., 1912, 10), reaching a maximum when the mixture contains about 42·5% by weight of the peroxide. This corresponds with a hydrate, N_2O_5,N_2O_4,H_2O, and the existence of this is confirmed by a thermal study of the reciprocal solubilities of nitric acid and nitrogen peroxide. This hydrate is stable below −48·5°, and at this temperature dissociates, liberating nitrogen peroxide.

Sulphuric acid is not appreciably soluble in nitrogen peroxide, but when added to anhydrous nitric acid or the acid containing a little water, it does not appreciably alter the solubility of the peroxide in the acid providing the mixture does not contain more than 30% of sulphuric acid, the water content being the principal factor of solubility. W. G.

Some Properties of Acid Phosphates. A. Joannis (*Compt. rend.*, 1919, **168**, 1202—1203).—Neither disodium hydrogen phosphate nor potassium dihydrogen phosphate absorbs gaseous or liquid ammonia, and ammonium dihydrogen phosphate only absorbs it very slowly. Similarly, in the absence of water, magnesium ammonium phosphate cannot be obtained from magnesium hydrogen phosphate. W. G.

Allotropy of Carbon. Maurice Copisarow (*Chem. News*, 1919, **118**, 301—304).—The polyatomicity of the carbon molecule is proved by (i) the existence of several forms of carbon which are chemically and physically distinct from one another, (ii) the high volatilisation point, (iii) the general theory of the solid state, (iv) the products of moist oxidation, (v) the combustion of carbon, and (vi) the *X*-ray spectrometric study of the modifications of carbon. In accordance with the theory of allotropy (this vol., ii, 279), carbon may exist in three forms: (*a*) a non-rigid, molecular configuration, some valencies of which are free, (*b*) a rigid, molecular configuration, some valencies of which are free, and (*c*) a rigid, molecular configuration, all valencies of which are fixed. From a consideration of the heats of combustion, products of oxidation, and the physical properties of the three forms of carbon, it is shown that amorphous carbon is represented by *a*, graphite by *b*, and diamond by *c*. Possible configurations in keeping with the above are drawn in the paper. J. F. S.

The Oxidation of Coal. Frederick Vincent Tideswell and Richard Vernon Wheeler (T., 1919, **115**, 895—902).

The Preparation of Carbonyl Chloride by Means of Carbon Tetrachloride and Oleum or Ordinary Sulphuric Acid. V. Grignard and Ed. Urbain (*Compt. rend.*, 1919, **169**, 17—20).—With sulphur trioxide, carbon tetrachloride reacts according to the equation $2SO_3+CCl_4=COCl_2+S_2O_5Cl_2$, but with pyrosulphuric acid the reaction is $SO_3+H_2SO_4+CCl_4=COCl_2+2SO_3HCl$. With ordinary sulphuric acid in the presence of

infusorial earth as a catalyst, the reaction is $2H_2SO_4 + 3CCl_4 = 3COCl_2 + 4HCl + S_2O_5Cl_2$, together with a slight secondary reaction, $S_2O_5Cl_2 + CCl_4 = COCl_2 + 2SO_2Cl_2$. The principal objection to this second method is the presence of hydrogen chloride with the carbonyl chloride, but this may be got over to some extent by dissolving the carbonyl chloride in carbon tetrachloride, the hydrogen chloride being only slightly soluble in this solvent. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. G.

Action of Concentrated Sulphuric Acid on Carbon Tetrachloride. Ch. Mauguin and L. J. Simon (*Compt. rend.*, 1919, **169**, 34—36. Compare Grignard and Urbain, preceding abstract).—Real sulphuric acid reacts with carbon tetrachloride at about 150° according to the equation $CCl_4 + H_2SO_4 = SO_3HCl + COCl_2 + HCl$. If an acid which is slightly aqueous is used, the water present is decomposed by the chlorosulphonic acid first formed, giving sulphuric acid and hydrogen chloride. Finally, the chlorosulphonic acid itself reacts with carbon tetrachloride, thus: $CCl_4 + 2SO_3HCl = S_2O_5Cl_2 + 2HCl + COCl_2$. The carbonyl chloride is purified by solution in carbon tetrachloride and subsequent distillation. W. G.

The Sulphones formed by the Iodides of Sodium, Rubidium, and Cæsium. R. de Forcrand and F. Taboury (*Compt. rend.*, 1919, **168**, 1253—1257).—By the action of liquid sulphur dioxide on the iodides of sodium, rubidium, and cæsium, the authors have obtained sulphones of the type $MI,3SO_2$, that of sodium being amorphous and the other two being soluble in excess of liquid sulphur dioxide, and crystallising from it on evaporation at 0°. W. G.

Stability of Sodium Thiosulphate Solutions. I. M. Kolthoff (*Pharm. Weekblad*, 1919, **56**, 878—888).—In general, the decomposition of thiosulphate solutions proceeds more rapidly in the light than in the dark. The oxidising action of the air may be prevented to some extent by covering the solution with a layer of light petroleum. The presence of alkaline substances prevents the decomposition almost completely. The addition of about 0·2 gram of sodium carbonate per litre is sufficient to ensure in great measure the stability of the solution. The accelerative effect of deposited sulphur on the decomposition is probably due to bacterial action. The decomposition may be retarded by the addition of 0·01 gram of mercuric iodide per litre of solution. W. S. M.

Sodium Hydrogen Sulphite Crystals ($NaHSO_3,3H_2O$).—Walther Schüler and Arno Wilhelm (*Zeitsch. angew. Chem.*, 1919, **32**, 198—199).—The sodium hydrogen sulphite crystals deposited at low winter temperatures from aqueous solutions contain three molecules of water. They are 2—6 cm. long, 2—3 mm.

thick, hexagonal in section, and belong apparently to the rhombic system. At higher temperatures or when removed from the mother liquor, they rapidly lose water and disintegrate, leaving a residue of anhydrous sodium hydrogen sulphite containing sulphate and traces of pyrosulphite if they have been exposed to the air.

G. F. M.

Lime Mortars: Solution and Conversion of Solid Substances into Colloids. V. KOHLSCHÜTTER and G. WALTHER (*Zeitsch. Elektrochem.*, 1919, **25**, 159—183).—The rate at which calcium oxide, prepared from calcium carbonate, calcium hydroxide, and calcium oxalate, respectively, combines with water vapour at the ordinary temperature has been determined. The volume changes and the amount of water taken up have also been determined. The rate of absorption is shown to differ with the various samples of calcium oxide. Further, the rate of sedimentation of calcium hydroxide has been measured for calcium hydroxide prepared by slaking lime in water or solutions of calcium chloride, calcium nitrate, sodium chloride, potassium chloride, potassium nitrate, sodium hydroxide, sodium acetate, potassium thiocyanate, ammonia, ammonium oxalate, and sodium carbonate of various concentrations. The rate at which sedimentation occurs varies with the different electrolytes; some when in small concentrations increase the sedimentation velocity, and in large concentrations decrease it, whilst in other cases the reverse is the case. The velocity of sedimentation is greater when water is added to quicklime than when lime is added to water. Further, a difference is observed in the rate of sedimentation of calcium hydroxide produced by slaking lime in lime-water. The sedimented product of a suspension of calcium hydroxide in water is not the same as the product obtained by slaking lime in water and allowing it to settle. The results obtained indicate that in the production of a true solution of calcium hydroxide in water from lime, an intermediate colloidal state is first formed. J. F. S.

Lead-Sodium-Mercury and Lead-Sodium-Tin Alloys. J. GOEBEL (*Zeitsch. anorg. Chem.*, 1919, **106**, 209—228).—A thermal investigation has been made of lead–sodium–mercury alloys containing up to 4% of sodium and 7% of mercury, and of lead–sodium–tin alloys containing up to 4% of sodium and 6% of tin. The lead–sodium binary alloys show a eutectic point at 308° with 2·7% of sodium, the eutectic consisting of mixed crystals of sodium and lead with a compound, probably Na_2Pb_5, which corresponds with 4% of sodium. To obtain the equilibrium diagram of the lead–sodium–mercury alloys, sixty-three fusions were made. In presence of mercury up to 2%, the lead–sodium eutectic persists, but the eutectic point is lowered about 5°. With more mercury, up to 7%, the eutectic point disappears, but is still represented in the diagram by a minimum in the same position. Sodium is more soluble in the lead–mercury mixed crystals than in pure lead. A

plan of the space diagram with isothermal lines is given. The series of fusions with 3% of mercury was extended up to 12% of sodium. The liquidus line rises from 2·7% to about 5% of sodium, then falls to a eutectic point between 7 and 8% of sodium at 290°, and again rises to a high maximum at 354° with 10% of sodium. It then falls rapidly towards another eutectic line at 280°. The existence of at least two compounds is indicated, but their nature is not apparent.

To obtain the equilibrium diagram for the lead–sodium–tin system up to 4% of sodium and 6% of tin, forty-eight fusions were made. The space diagram consists of two surfaces meeting in a depression running parallel to the lead–tin side of the diagram. This depression represents the separation of a eutectic consisting of lead–sodium mixed crystals with an unknown compound. The temperature of the eutectic point falls with increasing quantities of tin from 308° to 296°. The lead–tin mixed crystals appear to dissolve no more sodium than pure lead. E. H. R.

Reduction of Metallic Sulphides by Means of Aluminium. N. Parravano and P. Agostini (*Gazzetta*, 1919, **49**, i, 103—115. Compare Parravano and De Cesaris, A., 1917, ii, 292).—The displacement of the metal of a sulphide by another metal in accordance with the equation $M^1 + MS \rightleftharpoons M^1S + M$ is considered in the two cases: (1) when the reacting compounds are able to exist together without mixing, and (2) when such compounds are more or less miscible in the liquid state alone or in both the liquid and solid states.

In the experiments made, the metallic sulphide was added to molten aluminium contained in a clay crucible, the reacting substances being taken in weighed quantities. The fused mass was then gradually heated and stirred until reaction commenced, and after a short time was allowed to cool. In all cases, the apparatus was surrounded by an inert gas.

The sulphides investigated were PbS, Cu_2S, SnS, CdS, ZnS, Sb_2S_3, Ag_2S, Bi_2S_3, NiS, and CoS, all of which were largely, and some completely, desulphurised by aluminium. Noteworthy is the reduction of zinc sulphide, to which is attributed a higher heat of formation than to the equivalent proportion of aluminium sulphide. With PbS, Cu_2S, SnS, Ag_2S, and Bi_2S_3, the amount of the metal obtained approximates closely to the theoretical quantity, whereas this is not the case either (1) with CdS and ZnS, owing to the volatility of the reduced metal, or (2) with NiS and CoS, owing to projection of material from the crucible in consequence of the excessive vigour of the reaction. T. H. P.

New Synthesis of Phosgenite. W. A. Hamor and H. E. Gill (*Amer. J. Sci.*, 1919, [iv], **47**, 430).—Phosgenite, $PbCO_3,PbCl_2$, has been synthesised by heating a mixture of lead hydroxide and excess of carbonyl chloride for one to four hours at 95°, 120°, 150°, 175°, 200°, and 250°. The best results were

obtained at 175°, the amount formed being less the higher the temperature above this value. The product was crystalline and of a faint yellow colour, identical in all respects with the naturally occurring mineral. J. F. S.

Combinations of Mercuric Chloride and the Alkali Chlorides. C. Tourneux (*Ann. Chim.*, 1919, [ix], **11**, 225—361).—From a study of the equilibrium of the system mercuric chloride–potassium chloride–water at 34°, 56°, 80°, and 100°, the author shows that it is possible to obtain two crystalline salts having the composition $HgCl_2,2KCl,H_2O$ and $2HgCl_2,KCl,2H_2O$. In addition, three sets of crystals have been obtained, the composition of which may be represented by $(2HgCl_2,KCl,H_2O)_4(HgCl_2,2KCl,H_2O)$, $(2HgCl_2,KCl,H_2O)(HgCl_2,2KCl,H_2O)$, and $(2HgCl_2,KCl,H_2O)(HgCl_2,2KCl,H_2O)_4$.

The author is not certain as to whether the last three formulæ represent double salts or simply mixed crystals of the two salts the composition of which is expressed in the brackets. He has not succeeded in preparing the hydrate $2HgCl_2,KCl,H_2O$. He has verified the existence at the ordinary temperature of the following crystalline salts: $HgCl_2,RbCl,H_2O$; $HgCl_2,NaCl,2H_2O$; $HgCl_2,NH_4Cl,H_2O$; $4HgCl_2,3RbCl,H_2O$.

The crystalline double salts formed by mercuric chloride and the alkali chlorides are all homœomorphic and show a marked chemical analogy. The analogy of the properties of these crystals with those of the zeolites suggest that the water content of the crystals depends on the vapour tension of the surrounding medium. W. G.

Extraction of Gallium and Germanium from Zinc Oxide. H. C. Fogg and C. James (*J. Amer. Chem. Soc.*, 1919, **41**, 947—949).—Some zinc ores contain small, though appreciable, amounts of germanium and gallium, and, these metals being less volatile than zinc, remain behind in the retorts when the zinc distils off. These residues furnish a good source for the elements gallium and germanium, although the amounts obtainable vary enormously; for example, 100 lb. of one specimen gave 8 grams of pure gallium, whilst a second sample of 200 lb. yielded only the merest traces; the amount of germanium in the two samples was almost identical. One kilo. of the oxide prepared from the zinc residues was treated with 2400 c.c. of commercial hydrochloric acid in a large flask, the oxide being added in small portions to the acid to prevent caking. When all had dissolved, a little potassium chlorate was added carefully until, after vigorous shaking, oxides of chlorine were evolved. The flask was then connected to a condenser and a thermometer placed with its bulb in the liquid, and the liquid distilled; two fractions were collected, the first, up to 121°, containing very little germanium, and the second, up to 135—140°, containing practically the whole of the

germanium. The distillates from several quantities were then saturated with hydrogen sulphide, and the white sulphide filtered off. The liquid left in the flask was diluted with a litre of water and lead chloride allowed to settle. The clear liquid was decanted from the sediment and treated with ammonium hydroxide until a slight permanent precipitate was formed, metallic zinc was added, and the whole digested at the boiling point for several hours. The precipitation was considered complete when a portion of the supernatant liquid gave a precipitate of basic zinc chloride on dilution with water. The precipitated metals and basic salts were filtered off and the filtrate examined spectroscopically to ascertain if all the gallium had been precipitated. Ten such precipitates, corresponding with 30 kilos. of the original oxide, were united, dissolved in commercial hydrochloric acid with the aid of a little potassium chlorate, boiled, and lead chloride allowed to separate. This was removed and the solution saturated with hydrogen sulphide. The precipitate was filtered off and the filtrate boiled, neutralised with dilute ammonium hydroxide until a permanent precipitate just formed, and again digested with zinc at the boiling point. When the solution had turned basic, it was poured from the precipitate, diluted, and filtered, the operation being repeated with the filtrate until the basic precipitate ceased to show a gallium spectrum. The precipitates poor in gallium were placed with those first obtained from the crude zinc chloride. The precipitates rich in gallium were again dissolved in hydrochloric acid, the solution nearly neutralised, saturated with hydrogen sulphide, and filtered. The filtrate was treated with ammonium chloride, made alkaline to litmus with ammonia, and boiled until just acid. A gelatinous precipitate consisting of gallium, aluminium, and iron hydroxides was filtered off and washed. From 100 lb. of the crude zinc oxide, 60 grams of the mixture of hydroxides was obtained. These were dissolved in the minimum quantity of hydrochloric acid, diluted with water, and nearly neutralised with sodium hydroxide. After the addition of a little formic acid, the liquid was treated with an excess of sodium formate, the precipitate collected, and thoroughly washed to ensure the complete removal of zinc. The precipitate and filter paper were placed in water in a casserole, saturated with hydrogen sulphide, and digested with cold 1% hydrochloric acid. The insoluble tin and cadmium sulphides were removed by filtration. The filtrate was made slightly alkaline with ammonia, boiled until slightly acid, and the gallium and aluminium hydroxides filtered off. These were dissolved in the minimum quantity of hydrochloric acid, and an excess of sodium hydroxide solution added. The solution was then electrolysed by a current of 1·5 amperes, using platinum electrodes 3 cm. sq. The gallium was deposited on the cathode in bright, shining globules, which dropped off as they became larger. When no more gallium was deposited, the solution was poured off and the metal washed several times with water, and the globules then united by the addition of a few drops of concentrated hydrochloric acid. J. F. S.

Monoclinic Double Selenates of the Iron Group. A. E. H. TUTTON (*Phil. Trans.*, 1919, [*A*], **218**, 395—440).—The crystallographic and optical investigation of the crystals of the four salts of the series $R_2M(SeO_4)_2,6H_2O$, in which M is ferrous iron and R is potassium, rubidium, cæsium, and ammonium, has been completed, and the detailed results are recorded in this paper. The examination of the crystals of the potassium salt was accomplished under great difficulties on account of the rapid decomposition of the crystals, apparently into the dihydrate, at temperatures very little above 0°. Suitable crystals were obtained on four very cold nights, and the necessary measurements were made by intensive working in a room the temperature of which never exceeded 6°.

The salts all crystallise in the holohedral class of the monoclinic system, and are closely isomorphous with the other salts of this extensive series. In this group, as in other groups of the series, there is a regular progression in the habit and dimensions of the crystals from the potassium, through the rubidium, to the cæsium salt, whilst the ammonium salt approximates closely in most respects to the rubidium salt.

Potassium ferrous selenate, $K_2Fe(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7490:1:0{\cdot}5044$, $\beta=103°50'$, D_4^{20} 2·494, M.V. 210·39.

Rubidium ferrous selenate, $Rb_2Fe(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7424:1:0{\cdot}5000$, $\beta=104°57'$, D_4^{20} 2·800, M.V. 220·29.

Cæsium ferrous selenate, $Cs_2Fe(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7308:1:0{\cdot}4979$, $\beta=106°2'$, D_4^{20} 3·048, M.V. 233·21.

Ammonium ferrous selenate, $(NH_4)_2Fe(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7433:1:0{\cdot}5019$, $\beta=106°9'$, D_4^{0} 2·191, M.V. 220·39.

The regular, progressive change in the dimensions of the crystal structure in the isomorphous series on passing from potassium to cæsium is associated with the regular increase in the atomic number of the alkali metal. The isomorphism of the ammonium salts with those of the alkali metals is held to be proof of the invalidity of the Barlow-Pope theory of valency volume. E. H. R.

Triboluminescence of Uranium Compounds. J. A. SIEMSSEN (*Chem. Zeit.*, 1919, **43**, 267).—The author has made experiments with a number of samples of uranium nitrate in an attempt to obtain explosive crystals of the kind reported by Ivanov (A., 1912, ii, 455) and Andrews (A., 1913, ii, 60). In no cases were explosive crystals obtained, but generally they showed the property of triboluminescence. It is concluded that the explosive crystals observed by the above authors owed their property to the presence of a labile nitric oxide compound. The triboluminescence of uranium salts is attributed to electrical tension in the crystals. E. H. R.

Analytical Chemistry.

The Use of Freezing-point Determinations in Quantitative Analysis. Charles Edward Fawsitt (T., 1919, **115**, 801—808).

Calculation of Possible Error in Volumetric Analysis. V. Zotier (*Bull. Sci. Pharmacol.*, 1918, **25**, 274—282, 357—364; from *Chem. Zentr.*, 1919, ii, 636—639).—A mathematical paper in which the inaccuracies inherent in volumetric analysis are considered. The errors arise from incorrect calibration and reading errors in measuring vessels (pipette and burette) and from uncertainty with respect to the end-point of the indicator. The various methods of preparing standard solutions are also treated, as well as errors due to impurity in the standard substance. A mathematical expression taking these factors into account is derived, for details of which the original must be consulted. It is thus calculated that the possible error in the determination of chlorine in commercial salt (1 gram of substance dissolved in 100 c.c. and titration of 20 c.c. of the solution with $N/10$-$AgNO_3$) is about 1 in 100. H. W.

New and Rapid Apparatus for Electrochemical Analyses. J. T. King (*Chem. and Met. Eng.*, 1919, **21**, 25—29).—In electrochemical analyses, agitation of the electrolyte hastens deposition of the metal, and the author has originated a more efficient method of agitation by rotating the containing beaker. Two experimental designs and the final form of apparatus are described. Besides the method of stirring, the system of wiring and the electrode holders are novel. The circuit is not broken when a beaker is lowered and a cell removed from the circuit. The operation of the apparatus and the method of carrying out an analysis are described. Tests were made on copper solutions of known strength to determine the speed and accuracy of the apparatus, and the results are tabulated. With currents of three, six, and nine amperes, the times taken to deposit 1 gram of copper were found to be thirty-five, twenty-five, and sixteen minutes respectively. Three unknown brasses were analysed for copper, and the results obtained by this and other methods of stirring, and carried out by different operators, are tabulated, and show excellent agreement. T. H. B.

Comparative Tests of "Palau" and "Rhotanium" Ware as Substitutes for Platinum Laboratory Utensils. L. J. Gurevich and E. Wichers (*J. Ind. Eng. Chem.*, 1919, **11**, 570—573).—"Rhotanium A" ware (gold, 90%; palladium, 10%) is superior to platinum as regards resistance to loss on heating, boiling hydrochloric and hydrofluoric acids, boiling 20% sodium hydr-

oxide solution, sulphuric acid, and fusion with sodium carbonate or potassium pyrosulphate, but inferior as regards the action of nitric acid, ferric chloride solution, and fused sodium hydroxide. It must not be heated higher than 1100°. "Rhotanium C" (gold, 70%; palladium, 30%) and "palau" (gold, 80%; palladium, 20%) alloys are superior to platinum as regards heating up to 1200°; they behave towards reagents similarly to "rhotanium A," but are not suitable for potassium pyrosulphate and sodium hydroxide fusions. W. P. S.

Sulphite Leuco-derivatives of Triaminotriphenylmethane as Reagents for Alkalinity and for Dissociation of Salts. I. Guareschi (*Gazzetta*, 1919, **49**, i, 115—123).—Magenta and other colouring matters of the triphenylmethane group, when reduced by means of sulphur dioxide or a hydrogen sulphite, serve as good reagents for bromine and hypobromites (A., 1912, ii, 989), and it is now found that they are also applicable to the detection of alkalinity, particularly with potable waters. The constitution of these compounds still remains undecided (compare Hantzsch and Ostwald, A., 1900, i, 256). The sensitiveness of the reaction is such that preliminary concentration of the water by evaporation is unnecessary; the intensity of the coloration is greater when an ethyl group than when a methyl group is present in the leuco-derivative, and still greater when the ethyl group is united to an imino-group.

Decolorised triethylrosaniline hydrochloride (Hofmann's violet) gives an intense violet coloration with dilute solutions of faintly alkaline salts, such as calcium hydroxide, carbonate or hydrogen carbonate, dimetallic hydrogen phosphates, borates, lead salts (normal or basic acetate), sodium acetate, basic quinine sulphate, aniline, magnesium phosphate, and magnesium ammonium phosphate; the reaction is more sensitive than that with litmus or other indicator. Wheat starch, which contains no proteins, gives no coloration, whereas rice starch, always containing more or less protein matter, reacts distinctly. The colouring matter formed is highly adherent to glass. With distilled water, or with dilute solutions of neutral salts like sodium chloride, no reaction takes place within an hour, and only a very faint coloration appears after a long time.

Similar colorations are given by magenta, *p*-rosaniline hydrochloride, methyl-violet, and crystal-violet, previously decolorised by sulphur dioxide. The coloration of the crystal-violet reagent by hypochlorites (compare Le Roy, A., 1916, ii, 535) is given also by solutions having an alkaline reaction, but free from hypochlorite. T. H. P.

Estimation of Perchlorates, Alone, or in the Presence of Chlorates and Chlorides. J. Guilfoyle Williams (*Chem. News*, 1919, **119**, 8).—Perchlorates, but not chlorates, are reduced by titanium trichloride solution in hot acid solution. An

excess of titanium trichloride is used, and this excess is subsequently titrated with ferric sulphate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. P. S.

Estimation of Iodide in Mineral Waters and Brines. W. F. Baughman and W. W. Skinner (*J. Ind. Eng. Chem.*, 1919, **11**, 563—568).—A quantity of the sample containing not more than 0·1 gram of iodine or more than 10 grams of total salts is diluted to 100 c.c., boiled with the addition of sodium hydroxide and sodium carbonate, and filtered. The filtrate is neutralised with sulphuric acid, 1 c.c. of 4% sodium hydroxide solution is added, the mixture boiled, an excess of potassium permanganate is added, and this excess then decomposed by treating the cold mixture with alcohol. After filtration, the solution is treated with 2 grams of potassium iodide, acidified with hydrochloric acid, and the liberated iodine titrated with thiosulphate solution. If it is desired to estimate bromine in the sample, the iodine may be first separated by steam distillation with the addition of ferric sulphate; the distilled iodine is collected in potassium iodide solution and titrated. W. P. S.

A Modified "Etching" Test for Fluorides. William Partridge (*Analyst*, 1919, **44**, 234—235).—The substance under examination is treated with 2 or 3 c.c. of 25% (by volume) sulphuric acid, the liquid covered with a layer of butter fat, and the test-tube placed upright in water at 80° to 95° for three hours. In the presence of 0·01 gram of sodium fluoride, the glass in contact with the acid will be "etched," and the markings will not be affected by successive treatment with ether, boiling alcohol, and boiling hydrochloric acid, or by rubbing with a piece of wood. C. A. M.

Method of Analysis of Fluospar and of Basic Slags containing Fluorine. G. R. Doyle (*Chem. News*, 1919, **118**, 304—305).—Half a gram of the finely powdered sample is weighed into a dish, converted into a paste with 5 c.c. of water, and evaporated on a water-bath almost to dryness with 35 c.c. of glacial acetic acid. A further quantity of 25 c.c. of glacial acetic acid is added, and the mass evaporated to dryness on a water-bath and then heated in a steam-oven until all acid has been expelled. The residue is transferred to a beaker and diluted to 80 c.c., boiled, and filtered. The filtrate contains (*a*) available lime (CaO or $CaCO_3$), (*b*) soluble silica, (*c*) manganese, (*d*) magnesia, (*e*) lead, whilst the residue contains (*a*) all calcium existing as CaF_2, (*b*) silica, and (*c*) iron and alumina. The residue is ignited in a platinum dish, cooled, weighed, treated with hydrofluoric acid, evaporated to dryness, ignited, and weighed. The loss in weight gives the amount of silica present. The remaining residue is treated with 5 c.c. of sulphuric acid and evaporated until fumes are evolved, then it is ignited and weighed. The gain in weight is the increase of calcium sulphate over calcium fluoride, $CaSO_4 \times 0{\cdot}5735 = CaF_2$. The residue is boiled for twenty minutes

with 20 c.c. of hydrochloric acid, diluted, and precipitated by the addition of ammonium chloride and ammonia, boiled, filtered, ignited, and weighed. The weight is deducted from the weight of iron, aluminium, and calcium fluoride, and gives the weight of calcium fluoride. If lead is present, it must be removed by hydrogen sulphide before the iron and aluminium are precipitated. The filtrate is estimated in the usual way. J. F. S.

Estimation of the Oxygen Content of Organic Substances. Robert Strebinger (*Zeitsch. anal. Chem.*, 1919, **58**, 97—114).—Oxidation by heating at 200° with a mixture of potassium iodate and sulphuric acid, and subsequent iodometric titration of the excess of iodate, affords a means of estimating the oxygen content of organic substances provided that the percentage amounts of the other constituents are known. The method is applicable to substances containing carbon, hydrogen, oxygen, halogens, sulphur, and nitrogen, but the nitrogen must not be present as amide. The oxygen may be calculated from the following formula:

$$O\% = 2{\cdot}6666 \times C\% + (1 - 0{\cdot}21568 \times N\%/H\%) \times 7{\cdot}9369 \times H\% + 1{\cdot}497 \times S\% - 100 \times O'/E,$$

where E is the weight of substance and O' the quantity of oxygen yielded by the iodate; 6 molecules of iodate give 15 atoms of oxygen. W. P. S.

Estimation of Nitrogen and Ammonia as Ammonium Chloride. A. Villiers (*Bull. Soc. chim.*, 1919, [iv], **25**, 335—337. Compare A., 1918, ii, 332).—Further evidence is given showing that the loss in weight of ammonium chloride when heated in a narrow-necked, conical flask for four days at 105° is practically negligible (compare Auger, this vol., ii, 117). W. G.

Volumetric Estimation of Phosphoric Acid by the Pincus Method, as applied to the Estimation of Magnesium. J. W. Springer (*Zeitsch. angew. Chem.*, 1919, **32**, 192).—The magnesium salt is precipitated as ammonium magnesium phosphate, the precipitate heated to boiling with ammonium acetate solution and water, and titrated with standardised uranyl acetate solution, using potassium ferrocyanide as an external indicator. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. P. S.

Microelementary Analysis. E. Diepolder (*Chem. Zeit.*, 1919, **43**, 353—354).—Methods are described for the estimation of nitrogen, carbon, hydrogen, and halogens in very small quantities (a few mg.) of substance; the first three elements mentioned are estimated by combustion, whilst halogens are estimated by the Carius method. [See, further, *J. Soc. Chem. Ind.*, 1919, August.] W. P. S.

Micro-methods for the Determination of Carbon and Moisture in Minerals. G. Karl Almström (*Svensk. Kera. Tidskrift*, 1919, **31**, 71—74).—Pregl's apparatus for combustion

and his potassium dichromate were applied to the estimation of carbon dioxide and moisture in minerals. The moisture values obtained in this way were too high. Vanadium pentoxide, having a low m. p. (660°), being strongly acid at high temperatures and combining with most substances to give readily fusible products, was thought to be a likely substitute that might give better results. The results for carbon dioxide were accurate, but the moisture values were still too high. Twenty to thirty mg. of the sample were used, and to this was added 0·2 to 0·3 gram of the oxidising agent. Neither can be rendered sufficiently free from moisture to yield trustworthy results. A Penfield apparatus made on a "micro" scale gives trustworthy figures when employed in the estimation of moisture in minute amounts of mineral sample.

CHEMICAL ABSTRACTS.

Cyanometric Method of Estimating Silver and Halogens in Ammoniacal Solution. J. EGGERT and LOTTE ZEPFEL (*Ber.*, 1919, **52**, [*B*], 1177—1185).—The procedure depends on the fact that silver iodide is only precipitated from very dilute ammoniacal solutions of silver salts by addition of potassium iodide when large amounts of electrolytes are present or when the solution is warmed, continuously shaken, or preserved for a long time; otherwise, an opalescence of colloidal silver iodide is formed. If potassium cyanide solution is added, the turbidity increases at first and suddenly disappears when the amount of CN' necessary for the formation of $Ag(CN)'_2$ has been added. Silver is estimated in ammoniacal solution in the following manner. A known volume of approximately 0·1*N*-potassium cyanide solution is diluted with about four times its volume of water, and sufficient ammonia is added to make the solution at least 0·25*N*; after introduction of a quantity of potassium iodide approximately equivalent to that of the cyanide taken, the silver solution is added to incipient turbidity. Halogens are estimated indirectly by using an excess of silver nitrate solution and titration of the residual silver after filtration of the silver haloid. The method can also be applied for estimation of acids, the silver salts of which are distinguished by sufficient difference in their solubility in ammonia; thus, chloride and iodide may be simultaneously estimated in that their sum is determined by the indirect process and the iodide alone estimated in a solution which is sufficiently ammoniacal to retain the silver chloride in the dissolved state. To obtain accurate results, it is necessary that the amount of potassium iodide used as indicator should be approximately equivalent to the amounts of substance taken for titration.

The use of potassium iodide in Liebig's method of titration is shown to bring no advantage, and in certain cases even to lead to false results. H. W.

Sensitive Reaction of Manganese Salts. H. CARON and D. RAQUET (*Ann. Chim. anal.*, 1919, [ii], **1**, 174).—A red

coloration is obtained when 10 c.c. of a manganese salt solution is treated with 2 c.c. of saturated potassium oxalate solution, 1 c.c. of acetic acid, and a few drops of potassium hypochlorite solution. The test will detect the presence of as little as 0·05 mg. of manganese in 10 c.c. of solution. Zinc salts do not interfere with the reaction, but iron salts must not be present. W. P. S.

Estimation of Ferrous Iron by means of the Oxidation Potential. I. M. Kolthoff (*Chem. Weekblad*, 1919, **16**, 450—461).—The ferrous solution, acidified with sulphuric or hydrochloric acid, is titrated with a standardised potassium dichromate solution. The *E.M.F.* between a platinised platinum electrode immersed in the solution and a normal calomel electrode is determined after successive additions of the dichromate solution, and the values obtained are plotted in a curve against the volume of the solution added. In the neighbourhood of the end-point, the *E.M.F.* increases rapidly, the exact end-point being given by the middle point of the nearly vertical curve section. Titration with potassium bromate gives satisfactory results, the end-point being sharper in hydrochloric than in sulphuric acid solution. With potassium permanganate solution, the value of the *E.M.F.* obtained is variable, increasing when the liquid is stirred.
W. S. M.

Estimation of Nickel in Ferro-nickels and Steels. Paul Nicolardot and Georges Gourmain (*Bull. Soc. chim.*, 1919, [iv], **25**, 338—344).—A comparison of the three methods of estimating nickel in nickel steels, namely: (1) electrolytic method; (2) precipitation with dicyanodiamidine; (3) precipitation with dimethylglyoxime. Method (2) gives results comparable with those of method (3), but needs much more care in its conduct. The results obtained by the use of dimethylglyoxime are invariably lower than by the electrolytic method, since in the latter method any cobalt present, and generally a little iron and manganese, are weighed in with the nickel. For rapid work, too, the dimethylglyoxime method is preferable, the precipitate being weighed on a tared filter paper. W. G.

Estimation of Small Quantities of Antimony. W. Beam and G. A. Freak (*Analyst*, 1919, **44**, 196—199).—When modified slightly, a method described by Schidrowitz and Goldsbrough (A., 1911, ii, 338) was found to be trustworthy. In this method, the antimony is deposited on a strip of copper, then dissolved in alkaline permanganate solution, and estimated colorimetrically as sulphide. The chief modifications introduced are the reduction of antimony solution with sulphur dioxide before the precipitation with hydrogen sulphide (this ensures the precipitation of the metal as its trisulphide, which is always the case in the comparison solution), and the use of 1% potassium hydroxide solution and a limited amount of potassium permanganate solution for the solution of the

deposited antimony. [See, further, *J. Soc. Chem. Ind.*, 1919, 515A.] W. P. S.

Estimation of Small Amounts of Benzene in Ethyl Alcohol. F. W. Babington and Alfred Tingle (*J. Ind. Eng. Chem.*, 1919, **11**, 555—556).—One hundred c.c. of the alcohol are mixed with 200 c.c. of water and distilled, 20 c.c. of distillate being collected in a narrow, graduated tube having a capacity of 50 c.c. This distillate is treated with 15 c.c. of potassium dichromate solution (one-sixth saturated) and 2 c.c. of hydrochloric acid (D 1·12), the tube closed with a rubber stopper, and its contents mixed. After about fifteen minutes, the mixture is shaken with exactly 10 c.c. of light petroleum and the latter allowed to separate; the increase in volume of the petroleum gives the amount of benzene present. The method is trustworthy for quantities of benzene up to 0·75%. W. P. S.

Chlorination of Benzene. Analysis of Mixtures of Benzene, Chlorobenzene, and Dichlorobenzene, etc. Percy F. Frankland, S. Raymond Carter, and Dorothy Webster (*J. Soc. Chem. Ind.*, 1919, **38**, 153—155).—The method described is similar in principle to that employed by Colman (A., 1915, ii, 184; *J. Soc. Chem. Ind.*, 1919, **38**, 57) for the estimation of the percentages of benzene, toluene, and xylene in commercial toluene. The sample (100 c.c.) is distilled from an Engler flask under uniform conditions, and the distillates are collected in measuring cylinders. Three fractions are obtained by interrupting the distillation at 122° (corr.) and again at 142° (corr.). The volumes of liquid which distil below 122° and above 142° are noted, and the percentages of benzene and chlorobenzene present in the original mixture are obtained from a graph which has been constructed from experiments with mixtures of known composition. The dichlorobenzene may be found by difference. The graph is only applicable to samples containing 50—80% of chlorobenzene and for those which contain such amounts of benzene and dichlorobenzene as yield not less than 5% or more than 50% either below 122° or above 142°; in cases where the sample does not fall within these limits, such measured volume of benzene, chlorobenzene, or dichlorobenzene is added that the resulting mixture comes within the specified limits. The graph was constructed by the use of pure *p*-dichlorobenzene, but it is found that the presence of *o*-dichlorobenzene does not materially affect the accuracy of the process even if it forms about 40% of the total dichlorobenzene present in the mixture. Benzene hexachloride, if present, should be filtered before distillation, and the quantity then remaining in solution is too small to influence the analysis; if its percentage is required, it is allowed to separate at the ordinary temperature from the fraction, b. p. above 140°, collected, washed with light petroleum (b. p. 65°), and dried. The mother liquor is concentrated, and the second crop similarly treated and weighed with the first lot of benzene hexachloride. H. W.

Estimation of Monochlorobenzene in Mixtures containing Benzene, Monochlorobenzene, and Dichlorobenzene. N. G. S. Coppin and F. Holt (*Analyst*, 1919, **44**, 226—229).—A method of estimating monochlorobenzene in crude chlorinated benzene has been based on Northall-Laurie's method of estimating toluene in commercial toluene (A., 1915, ii, 703). A known volume of the sample is distilled, the first quarter of the distillate collected, a further half then distilled, and the residual quarter left in the flask. The boiling points of the first fraction and of the residue are determined in the special apparatus devised by Northall-Laurie, and from these results, by reference to a graph constructed from the results obtained with mixtures of known composition, the amount of monochlorobenzene in the sample is found. The graph is made by plotting the results obtained with weighed quantities of benzene, monochlorobenzene, and *p*-dichlorobenzene, the boiling points of the first fractions forming the ordinates and those of the residues the abscissæ. Small amounts of *o*-dichlorobenzene and trichlorobenzene are also formed when benzene is chlorinated, but not in sufficient quantity to have a material influence on the results. [See, further, *J. Soc. Chem. Ind.*, 1919, August.]

C. A. M.

A Revision of the Copper Phosphate Method for the Titration of Sugar. Otto Folin and Eugene C. Peck (*J. Biol. Chem.*, 1919, **38**, 287—291).—Variable results were encountered with this method when salt mixtures prepared from the same lot of chemicals by different individuals were employed. It was ascertained that, in order to obtain concordant results, great care must be taken to prepare the salt mixture correctly. The preparation of this mixture is described in detail. The method of Folin and McEllroy (A., 1918, ii, 207) could, however, be justly criticised on the ground that reduction of the copper sulphate by the thiocyanate may occur. By rendering the copper sulphate solution alkaline before adding the thiocyanate, this reduction is prevented. The modified process is as follows: 5 c.c. of the 5·9% copper sulphate solution are placed in a test-tube and rendered alkaline by the addition of 1 c.c. of saturated sodium carbonate. Four to five grams of the phosphate–carbonate–thiocyanate mixture are now added, and the whole is heated until the salts have dissolved. The titration is then carried out as described in the original method.

J. C. D.

Micro-estimation of Sugar in Blood. A. Kowarsky (*Deut. med. Woch.*, 1919, **45**, 188—190; from *Chem. Zentr.*, 1919, ii, 475).—The method depends on Bertrand's process, which consists in boiling the sugar solution with alkaline cuprous oxide solution, separating the precipitated copper oxide from the solution, and dissolving it in acidified iron sulphate solution; the ferrous oxide formed (equivalent to the cuprous oxide) is titrated with permanganate. To avoid loss when working with small quantities of

sugar, a known weight of the latter is added to the cuprous solution, which is subsequently deducted from that found experimentally. The method permits an exact estimation of sugar (to 0·01%) in 0·35 c.c. of blood, and can also be used for determining sugar in urine. It is particularly useful in diagnosis of disease of the kidneys, in which only small quantities of urine are frequently available; an exact estimation can be made with 0·1 c.c. of urine.

H. W.

New Method for the Estimation of Oxalic Acid. Hugo Krause (*Ber.*, 1919, **52**, [*B*], 1222—1223. Compare this vol., ii, 203).—A reply to Ott (this vol., ii, 303). H. W.

Methods for the Quantitative Estimation of Hippuric Acid. New, Simple, and Accurate Method. Eduardo Filippi (*Arch. Farm. Sperim. sci. aff.*, 1918, **26**, 243—256; from *Chem. Zentr.*, 1919, ii, 472).—A review of the previous methods is given, but the results obtained by them are not satisfactory. A simple method has therefore been elaborated based on the observation of Pelouze, that hippuric acid is converted into benzoic acid when boiled with sulphuric acid and manganese dioxide. Urine (300—500 c.c.) is concentrated to 100 c.c. and extracted during two hours at 60—65° with a mixture of benzene (2 volumes) and alcohol-free ether (1 volume); after removal of the solvent, the residue is heated under a reflux condenser, gently at first, but finally more strongly, with sulphuric acid (20 c.c.) and manganese dioxide (3—4 grams) during one and a-half hours. The product is distilled with steam, and the distillate is thoroughly extracted with ether. The benzoic acid left after removal of the ether is weighed. H. W.

Micro-estimation of Fat. E. and (Mrs.) F. Weehuizen (*Pharm. Weekblad*, 1919, **56**, 810—822).—A criticism of the method of Ivar Bang for the estimation of fat in small quantities of blood (Methoden zur Mikrobestimmung einiger Blutbestandteile). The following improvement of the method is proposed: About 0·3 gram of blood is absorbed in two or three pieces of filter paper (16 mm. × 26 mm.), and the weight determined in a torsion balance. The papers are dried in a vacuum and then placed in a test-tube (2·5 cm. × 16 cm.) with about 7 c.c. of alcohol. The tube is suspended in a water-bath at 90°, and the alcohol boiled for five minutes. The solution is transferred to a pointed centrifuge tube (1·5 × 10 cm.) and evaporated to 2·5 c.c. in a water-bath. The papers are extracted again with 8 c.c. of alcohol, and the solution is added to the centrifuge tube, in which the volume is again reduced to 2·5 c.c. In both cases, evaporation is expedited by passing hydrogen through a capillary tube into the liquid. Five drops of *N*/2-sodium hydroxide solution are now added, and the evaporation is continued until the volume is reduced to 0·3 c.c. As the duration of the saponification must be at least twenty

minutes, it may be necessary to add ten drops of alcohol and a drop of water when a volume of 1 c.c. is reached. The residue, which must be free from alcohol, is made up to 5 c.c. and is transferred to a micro-burette. The solution is used to titrate 1 c.c. of the standard calcium chloride solution until a permanent froth is obtained. The standard solution is prepared by adding 5·9 c.c. of $N/10$-calcium chloride solution to 13 grams of sodium chloride and making up to 1 litre. One c.c. of this solution is equivalent to 0·312 mg. of triolein. W. S. M.

Schiff's Reaction for the Detection of Carbamide. Domenico Ganassini (*Arch. Farm. sperim. sci. aff.*, 1918, **26**, 238—242; from *Chem. Zentr.*, 1919, ii, 473).—Schiff's reaction does not occur with pure furfuraldehyde. Acetone was found to be the active constituent of an efficient sample of furfuraldehyde. The reaction is obtained with certainty with a reagent of the following composition: furfuraldehyde (5 drops), acetone (2 c.c.), water (2 c.c.), and concentrated hydrochloric acid (1 c.c.). When a small quantity of this reagent is added to a minimal amount of carbamide, a pink coloration is gradually developed which becomes red and then intensely purple, and later brown. If acetone is replaced by other substances containing the COMe-group, such as ethyl acetate, acetaldehyde, acetylacetone, or pyruvic acid, red to violet colorations are more or less slowly developed, which, however, are indefinite and not to be compared with the beautiful coloration in the presence of acetone. H. W.

Estimation of the Amylolytic Power of Saliva. L. Grimbert (*J. Pharm. Chim.*, 1919, [vii], **19**, 244—250).—A quantity of air-dried potato starch equivalent to 5 grams of dry starch is boiled for two minutes with 100 c.c. of water, then cooled, 4 c.c. of filtered saliva are added, and the mixture is kept at 37° for one hour; it is then heated at 100° for ten minutes, cooled, diluted to 200 c.c., filtered, and the maltose is estimated in the filtrate. The amount of maltose is multiplied by 0·9473 to give the quantity of starch saccharified, and this, expressed as a percentage of the total starch, gives the amylolytic power of the saliva; for normal saliva, it lies between 73 and 74. W. P. S.

Value of Some New Colour Reactions of Urine. Alex. Skutetzky and M. Klaften (*Wien. klin. Woch.*, 1918, **31**, 1016—1018; from *Chem. Zentr.*, 1919, ii, 8).—The reactions proposed by Russo (methylene-green reaction), Wiener, and Kronberger have been critically examined; in each case, the coloration observed is due to simple physico-chemical causes, and does not depend on chemical processes. The reactions are consequently without diagnostic value. H. W.

General and Physical Chemistry.

The Infra-red Spectrum of Iron. H. M. Randall and E. F. Barker (*Astrophys. J.*, 1919, **49**, 42—47).—The region investigated extended from 9000 to 30,000 Å., and was found to contain some fifty measurable lines. The experimental arrangement was the same as that previously described (Randall, A., 1910, ii, 1014). The slit of the collimator and the thermopile were at first approximately 0·2 mm. wide, and covered a region in the neighbourhood of 1 μ of about 6 Å. and at 3 μ of about 3·7 Å. Later the entire spectrum was examined with a slit 0·5 mm. wide, and a very appreciable number of weaker lines were found and measured. No systematic differences between the values of wave-lengths measured with the slits of different width were noted. The material used in the major part of the work was ingot iron (99·8% Fe), the largest single impurity being copper, approximately 0·04%. Electrolytic iron also was used. No lines due to impurities in either were observed. The iron was placed in a boring in the positive carbon (1·9 cm.), the hole being as large as the carbon would permit. The carbons showed several infra-red potassium lines and also two others, the approximate values of which are 11,439 Å. and 10,692 Å. The origin of these lines is not known. The current used was in general greater than 60 amps. Tables of wave-lengths are given in Ångström units, as measured in air according to the Rowland scale. The relative intensities of the lines were estimated from the galvanometer deflexions. For the region between 0·8 μ and 1 μ the photographic method is more sensitive than the bolometric, but beyond 1 μ the latter becomes increasingly the more sensitive.

Chemical Abstracts.

The Infra-red Spectra of Cobalt, Nickel, Manganese, and Chromium. H. M. Randall and E. F. Barker (*Astrophys. J.*, 1919, **49**, 54—60. Compare preceding abstract).—The experimental arrangement and methods were the same as those for the iron spectrum. With the exception of manganese, which volatilised readily and gave a comparatively steady arc, the metals were very similar to iron in their action in the arc. Nickel and cobalt produced possibly an even more uncertain arc than iron. The strongest lines were given by manganese. The materials used were "pure" metals of commerce. No lines due to any of the impurities likely to be found were actually observed. The currents used were 60—80 amps. The spectrum of each metal was in general searched twice, once with narrow slits and once with double width slits. A number of the lines in the tables are multiples of strong lines of short wave-lengths. It is thought, however, that in each case it has been established that the higher order line of short wave-length is superposed by a line of long wave-length of the first order.

Chemical Abstracts.

The Applications of Beer's Law in Organic Chemistry. E. J. E. HÜFFER (*Chem. Weekblad*, 1919, **16**, 720—734).—A discussion of Beer's law of light absorption and its application to the determination of various cases of isomerism and polymerism in organic chemistry. Special reference is made to the colour theory of Hantzsch. W. S. M.

The *X*-Ray Spectra of the Elements. M. DE BROGLIE (*Compt. rend.*, 1919, **169**, 134—136).—The author has measured the frequency difference of the α- and β-rays in the *K*-spectrum of rhodium, and from these values has calculated the fundamental frequency of interval of Sommerfeld (*Ann. Physik*, 1916). He obtains the value $\Delta\nu_H=0{\cdot}369$, which is in close agreement with Paschen's figure (*loc. cit.*).

He has measured the wave-lengths of the first two *L*-bands in the absorption spectrum of radium, the results being: band L_1, $\lambda=0{\cdot}802\times10^{-8}$ cm.; band L_2, $\lambda=0{\cdot}670\times10^{-8}$ cm. The latter figure is a correction of one previously given (compare this vol., ii, 207). W. G.

Relation between General *X*-Radiation and the Atomic Number of the Target. W. DUANE and T. SHIMIZU (*Physical Rev.*, 1918, **11**, 491—492).—The intensity of the general *X*-radiation is proportional to the atomic number, and not to the atomic weight of the radiator. The apparatus used was a rotating target on which were mounted quadrants of iron, cobalt, nickel, and copper. The current produced by ionisation in a chamber containing methyl iodide was:

	Ion-current (volts/sec.).			
Volts.	Cu (29).	Ni (28).	Co (27).	Fe (26).
19,140	0·0124	0·0120	0·0114	0·0110
32,400	0·1327	0·1295	0·1251	0·1210

The numbers in parentheses are the respective atomic numbers. Cobalt occupies a position between iron and nickel, according to its atomic number as determined by Moseley, but not according to its atomic weight, which is anomalous. CHEMICAL ABSTRACTS.

The Structure of Radioactive Elements. INGO W. D. HACKH (*Physical Rev.*, 1919, **13**, 165—170).—Partial atomic structures of the elements in the periodic table between uranium and lead, on the basis of the radioactive disintegration series, are suggested. The emission of the α-particle causes the change of position of two electrons from the valency ring to an interior unstable ring, and the emissions of the β-particle the change of one electron in the opposite sense. This is referred to as a theory of metastasic electrons, and it supports the view that the seat of disintegration is not in the outer or valency shell, but in the next inner shell, and is caused by the shifting of two electrons. F. S.

"Old Age" of Chemical Elements. INGO W. D. HACKH (*Science*, 1919, **49**, 328—329).—A discussion based on Richards'

work on radioactive lead (A., 1914, ii, 453; 1917, ii, 91). The author states that "all other elements should be subject to an increase in mass, and it could therefore be predicted that, for example, helium of the atmosphere and of minerals will have an 'atomic weight' which is 0·0214 higher than the atomic weight of helium from radioactive disintegration, that is, there should be an 'old' or 'common' helium with atomic weight of about 3·94, and a 'neo' helium of atomic weight 3·92."

CHEMICAL ABSTRACTS.

Phenomena of Electrolytic Luminescence shown by certain Metallic Anodes. I. JAMES LAVAUX (*Compt. rend.*, 1919, **169**, 180—182).—Certain metals capable of giving, with the electrolytic anion, insoluble, adherent salts, which are non-conductors, show luminous phenomena correlative with a state of intense anodic polarisation. Of the metals studied, iron, copper, cadmium, and lead do not show any luminous phenomena and show no tendency to anodic polarisation. On the other hand, aluminium, magnesium, zinc, and bismuth show both. The luminous phenomena may be of two types, namely, phosphorescence and sparking. The first three metals show both types, but bismuth only shows sparking. The phenomena of electrolytic phosphorescence only appear in very short electric fields of high intensity, and are connected with high polarisation of the anode and the creation at its surface of an intense electric field. The phosphorescence is not accompanied by noise or sparking, and only occasions a minute expenditure of current and a very feeble development of heat. On the other hand, the sparking appears to characterise an abnormal working of the apparatus. It occurs in two forms: (1) more or less numerous, small, brilliant sparks; (2) a rain of fire giving the anode the appearance of a star-spangled sky in a state of continuous transformation. The sparking is due to the momentary rupture of the isolating layer at points where, for a few moments, a current sufficiently intense to volatilise a liquid film passes, whence interruption, sparking, and crepitation.

Of the four metals exhibiting these phenomena, aluminium is the best for their study. W. G.

The Melting Points of Mixtures of Organic Compounds. RICHARD MEYER and WILHELM MEYER (*Ber.*, 1919, **52**, [*P*], 1249—1255).—The melting point of an organic compound is, in general, depressed by admixture with a second substance; the authors have previously shown that this is not the case with the tribromo-compounds of mesitylene and ψ-cumene (this vol., i, 72), and now describe a series of similar observations with the following compounds: tetrabromo-*o*-xylene and tetrabromo-*m*-xylene; tetrabromo-*m*-xylene and tetrabromo-*p*-xylene; tetrabromo-*o*-xylene and tetrabromo-*p*-xylene; tetrabromo-*o*-, -*m*-, and -*p*-xylenes; dibromodurene and dibromo*iso*durene; thiophen picrate and thionaphthen picrate; thionaphthen picrate and naphthalene picrate; thiophen

picrate and naphthalene picrate; α- and β-methylnaphthalene picrates; β-methylnaphthalene and naphthalene picrates; monochloro- and monobromo-hydroxyhydrindenes. The phenomena have been more exhaustively investigated with the methylnaphthalene picrates and with naphthalene and β-methylnaphthalene picrates. The melting points of synthetic mixtures were determined in capillaries on the one hand and by determining the temperature of solidification on the other, similar, but not identical, results being obtained by either method. In the case of naphthalene and β-methylnaphthalene picrates, a depression is not observed, but the melting point rises sharply when more than 33% of the former is present; with α- and β-methylnaphthalene picrates, a slight depression occurs until the concentration of the former attains about 16%, after which the melting point rises. In both cases, the authors consider that mixed crystals are formed. H. W.

A Modification of the Freezing-point Method for the Determination of Molecular Weights. H. J. Prins (*Chem. Weekblad*, 1919, **16**, 929—931).—The determination of the molecular weight of substances containing hydroxyl by means of the depression of the freezing point in benzene solution is rendered difficult owing to the association of the solute. In such cases, a number of freezing-point measurements are made, each after successive additions of about 2 c.c. of benzene from a burette. The degree of association decreases with increasing dilution, and the true molecular weight is easily obtained by graphical extrapolation. W. S. M.

A New Form of Distilling Bulb. J. S. McHargue (*J. Ind. Eng. Chem.*, 1919, **11**, 670—671).—A new form of distilling bulb can be made from sections of glass tubing of different diameter. A bulb is blown on the end of the larger tube, and in the base of this a hole is blown to receive the top of the smaller tube, which has been made in the form of a T-tube with its arms open and deflected downwards. This is sealed into the tube, two small openings being left near the ends of the T-piece to allow condensed water to flow back into the interior of the distilling flask. The other end of the larger tube is bent twice at right angles, and is connected with the condenser. By the use of this bulb, soap bubbles are broken up, and the contents of the distilling flask cannot be carried over mechanically. A further advantage is that the steam issuing from the two ends of the T-piece into the bulb keeps the latter at a uniform temperature and accelerates the distillation. C. A. M.

The Density of the Saturated Vapour of Propyl Acetate and the Density of the Liquid which Emits this Vapour. E. Ariès (*Compt. rend.*, 1919, **169**, 216—219).—In the formulæ previously given for the molecular volumes of the saturated vapour and the liquid which emits it (see this vol., ii, 184), the values of the function *a* were not known. The author now deduces a formula

for calculating the values of a, and by means of it calculates the values of v_1 and v_2 for propyl acetate over a temperature range from 90° to 276·2°. The results are in close accord with those observed by Young. W. G.

The Use of Turpentine Resin in Turpentine as a Foam Breaker. E. C. Kendall (*J. Biol. Chem.*, 1919, **38**, 529).—A 20% solution of resin in turpentine is a most efficient foam breaker. The solution should be neutral to alizarin. J. C. D.

Equilibrium in the System Na_2SO_4–$CuSO_4$–H_2SO_4–H_2O. H. W. Foote (*J. Ind. Eng. Chem.*, 1919, **11**, 629—631).—At a given temperature, univariant systems of three components have two solid phases in equilibrium with a solution of definite composition and vapour pressure, whilst in the case of systems of four components there are three solid phases at such points. To determine the univariant points in systems of three components, a series of crystallisations at the given temperatures was made. When one compound was deposited near the point where another was formed an excess of the latter, or in some cases of both compounds, was added, and the solubility of the mixture determined. After the univariant points in a ternary mixture had been obtained, the corresponding points in a quaternary mixture were found by adding an excess of the third solid. In determining the changes which take place when sulphuric acid is added in increasing amounts, up to 60%, to the system Na_2SO_4–$CuSO_4$–H_2O, the solubilities of the univariant systems were determined, and the points graphically represented were connected with straight lines to show the composition of the corresponding bivariant systems. In the case of solutions containing the four components, copper was estimated electrolytically, sodium as sulphate after removal of the excess of sulphuric acid by ignition with ammonium carbonate, and free sulphuric acid by titration with sodium hydroxide solution.

System Na_2SO_4–H_2SO_4–H_2O.—The results obtained at 25° agreed substantially with those of D'Ans (A., 1906, ii, 351), although no evidence of the formation of the hydrate, $Na_3H(SO_4)_2,H_2O$, which D'Ans found to be rarely formed, was obtained. At 12°, the following compounds separated: $Na_2SO_4,10H_2O$, $Na_2SO_4,10H_2O$ and $Na_3H(SO_4)_2$, $Na_3H(SO_4)_2$ and $NaHSO_4,H_2O$, $NaHSO_4,H_2O$. At 25°, the solubility relationships are more simple, for at 12° the anhydrous salt is not stable under any conditions, and the decahydrate exists in equilibrium with the salt $Na_3H(SO_4)_2$ at the univariant point (see also Pascal, A., 1917, ii, 248).

System $CuSO_4$–H_2SO_4–H_2O.—In this system no acid salt is formed, but the sulphuric acid dehydrates the pentahydrate, yielding successively the trihydrate, monohydrate, and, finally, the anhydrous salt, in concentrated sulphuric acid.

System Na_2SO_4–$CuSO_4$–H_2O.—A transition temperature was observed at 16·7°, below which only a single salt crystallised. At 12° there is only a univariant system with two solid phases,

$Na_2SO_4,10H_2O$ and $CuSO_4,5H_2O$. At 25° there are two such systems, in one of which the solid phases consist of the double salt $Na_2SO_4,CuSO_4,2H_2O$ and $CuSO_4,5H_2O$, whilst in the other they consist of the double salt and $Na_2SO_4,10H_2O$.

System Na_2SO_4–$CuSO_4$–H_2SO_4–H_2O.—At 12° the two salts in water crystallise separately, but when more than 7·4% of sulphuric acid is present, the double salt forms, and at this concentration the univariant system contains the three solid phases of the two single salts and the double salt. In the presence of this proportion of sulphuric acid, the double salt is stable below its transition temperature. Equilibrium in the system $CuSO_4,5H_2O$–$Na_2SO_4,10H_2O$–double salt is reached very slowly at 12°, and the two single salts can remain in contact with a solution containing more than 7·4% of sulphuric acid for a considerable time without forming the double salt. The other systems soon attained equilibrium. At 12° the solid phases were as follows: (1) $Na_2SO_4,10H_2O$, $Na_3H(SO_4)_2$, double salt with 16·50% sulphuric acid in solution. (2) $Na_3H(SO_4)_2$, $NaHSO_4,H_2O$, double salt with 27·97% sulphuric acid. (3) $NaHSO_4,H_2O$, double salt (bivariant) with 58·2% sulphuric acid. (4) $CuSO_4,5H_2O$, $CuSO_4,3H_2O$, double salt with 50·54% sulphuric acid. (5) $CuSO_4,3H_2O$, $CuSO_4,H_2O$, double salt with 59·96% sulphuric acid. (6) $Na_2SO_4,10H_2O$, $CuSO_4,5H_2O$, double salt with 7·40% sulphuric acid. The results obtained at 12° and 25° are plotted in diagrammatic form, and show the instability of the sodium hydrogen sulphates in presence of copper sulphate, which converts them into the double salt.

C. A. M.

Action of Sulphuric Acid on certain Organic Compounds of Homologous and Isomeric Series. Jaroslav Milbauer and Antonín Němec (*J. pr. Chem.*, 1919, [ii], **99**, 93—105).—The authors have made experiments to ascertain the influence exerted by the constitution of organic compounds on the velocity of their oxidation by sulphuric acid. In each case, 4×10^{-4} gram-mols. of the compound were heated with 25 c.c. of the concentrated acid, this giving a column of liquid 9·5 cm. in height. The temperature was usually kept at 200°, but in some cases in which the velocity of reaction was very low, temperatures as high as 290° were employed. The sulphur dioxide formed was expelled by means of a current of carbon dioxide and its amount determined.

The aldoses are more difficult to oxidise than the corresponding polyhydroxy-derivatives, with the exception of mannitol, which in very small amounts (0·00004 mol.) retards the combustion of carbohydrates, without, however, affecting the final stage reached; mannitol thus acts as a true negative catalyst. The methylated carbohydrates undergo more profound combustion than the corresponding aldoses or alcohols containing the same number of carbon atoms; increase in the number of hydrogen atoms united to a carbon atom is accompanied by increase in the amount of sulphur dioxide formed. With isomeric sugars, steric configuration has no

influence on the combustion, and with di- and tri-saccharides, although these are not completely burnt, the amount of sulphur dioxide formed is equal to the sum of the amounts yielded by the constituent monosaccharides; the latter also do not undergo complete combustion. Mercuric sulphate not only acts as a positive catalyst, but increases the total quantity of sulphur dioxide; with 0·0001 gram-mol. of the salt, the increase amounts to 9% in the case of sucrose.

Dicarboxylic acids of the type $CO_2H\cdot[CH_2]_n\cdot CO_2H$ give with sulphuric acid at 200° only small amounts of sulphur dioxide, this resulting from decomposition of the acids with formation of carbon dioxide and monoxide, followed by reaction of the latter with the sulphuric acid, $CO + H_2SO_4 = CO_2 + SO_2 + H_2O$.

The unsaturated acids are very easily attacked, scission occurring first at the double linking. Aliphatic acids, such as oleic and fumaric acids, are oxidised far more rapidly than aromatic acids like cinnamic acid; aromatic hydroxy-acids (salicylic) are not oxidised by sulphuric acid at 200°. With the dicarboxylic acids of the aliphatic series, neither the velocity of combustion nor the amount of sulphur dioxide formed depends on the number of hydroxy-groups in the molecule, the reaction being determined in each case by the special chemical structure of the acid; here also mannitol acts as a true negative catalyst, whilst mercuric sulphate not only accelerates the oxidation, but carries it to a further extent.

With the amino-acids, the quantity of sulphur dioxide formed and the velocity of the combustion increase with the molecular weight; mannitol, and also boric anhydride, act as negative catalysts, and mercuric sulphate exerts the action described above. In the case of the aromatic hydrocarbons, the combustion proceeds further as the number of carbon-containing groups attached to the benzene nucleus increases.

Of the dihydroxybenzenes, the para-compound is oxidised the most rapidly and the meta-compound the most slowly, this behaviour being analogous to the reducing powers of these compounds when employed as photographic developers. None of the trihydroxybenzenes is oxidised as rapidly as it would be if one of the three hydroxy-groups were removed, but the rule holding with the dihydroxy-derivatives is obeyed; thus, pyrogallol represents a combination of two ortho-positions, hydroxyquinol one of an ortho- and a meta-position, and phloroglucinol one of two meta-positions. α-Naphthol is more rapidly oxidised than β-naphthol. With the quinones, the combustion is the more rapid the smaller the number of substituent groups in the $O{:}C_6H_4{:}O$ nucleus. T. H. P.

Derivation of the Law of Even Atomic Numbers. Ernst Mohr (*J. pr. Chem.*, 1919, [ii], **99**, 106—108).—If in any molecule the numbers of uni-, bi-, . . . sexa-valent atoms are a, b, . . . f respectively, the sum of all the valencies is given by $\Sigma V = a + 2b + 3c + 4d + 5e + 6f$. On the assumption that no valency in the mole-

cule remains unsaturated, the sum of all the linkings in the molecule is represented thus: $\Sigma B=\Sigma V/2=b+2d+3f+(a+3c+5e)/2$. Since both ΣB and $(b+2d+3f)$ are positive integers, the term $(a+3c+5e)/2$ must also be a positive integer. Further, as $(c+2e)$ is a positive integer, the expression $(a+3c+5e)/2-(c+2e)$, that is, $(a+c+e)/2$, must also be a positive whole number, and $(a+c+e)$ a positive, even integer; this is the law of even atomic numbers. A similar proof holds for the case when septa- and octa-valent atoms are present in the molecule.

With substances like triphenylmethyl, $C_{19}H_{15}$, in the molecule of which one valency is unsatisfied, the law holds only if one of the carbon atoms is regarded as tervalent.

This law is often useful in indicating the possibility or otherwise of particular molecular formulæ. T. H. P.

Inorganic Chemistry.

The Solubility of Iodine in Water-Alcohol Mixtures. N. Schoorl and A. Regenbogen (*Pharm. Weekblad*, 1919, **56**, 538—545).—The results of solubility determinations of iodine in water–alcohol mixtures as given in the literature are generally much too high, on account of the formation of hydriodic acid during the prolonged contact of the iodine with the solvent. The authors eliminate this source of error by preparing a nearly saturated solution of iodine in absolute alcohol. A weighed quantity of this is mixed with a weighed quantity of water, and, after shaking, a portion of the solution is drawn through a filter into a pipette and weighed. Potassium iodide solution is added and the iodine titrated with thiosulphate. W. S. M.

Effect of a Film of Oil on the Aeration of Water. Herbert F. Stephenson (*Analyst*, 1919, **44**, 288).—Water covered with a layer of petroleum oil 0·6 cm. in depth absorbs oxygen from the atmosphere at the same rate as does water not covered by oil. W. P. S.

Fluorosulphonic Acid, Fluorosulphonates, and Sulphuryl Fluoride. Wilhelm Traube, J. Hoerenz, and F. Wunderlich (*Ber.*, 1919, **52**, [*B*], 1272—1284).—It has been previously shown that ammonium fluorosulphonate can be prepared by the action of sulphur trioxide on ammonium fluoride (A., 1913, ii. 947); the further investigation of this and similar substances is described in the present communication.

Ammonium fluorosulphonate is most conveniently prepared by the gradual addition of dry ammonium fluoride to sulphuric acid

containing about 70% of sulphur trioxide, and treatment of the product with a small excess of ammonia dissolved in methyl alcohol. The salt has m. p. 245° and readily reacts with gaseous ammonia, particularly at low temperatures, with formation of liquid ammines. The alkali fluorosulphonates are prepared by the action of the requisite alkali hydroxide on the ammonium salt in aqueous solution; the *potassium* salt, short, stout prisms, m. p. 311°, the *rubidium* salt, m. p. 304°, the *lithium* salt, long, shining needles ($+3H_2O$), m. p. 60—61° or m. p. about 360° (anhydrous), are described. All the fluorosulphonates are freely soluble in water, with the exception of the *nitron* salt. The *barium* salt was not obtained in the pure form. The fluorosulphonates are unexpectedly stable towards water, from which they can be crystallised if the operation is rapidly performed; in the presence of mineral acids, they are readily hydrolysed to hydrofluoric and sulphuric acids, but are much more stable in alkaline solution. With aqueous ammonia, they yield chiefly aminosulphonates (compare this vol., i, 434).

The alkali fluorosulphonates are very stable towards heat; thus, when the potassium salt was heated for some time to bright redness, it only suffered slight decomposition, with the evolution of sulphur dioxide, sulphur trioxide, hydrogen fluoride, and oxygen. Crude barium fluorosulphonate, on the other hand, is decomposed at a red heat into barium sulphate and sulphonyl fluoride, this being the most convenient method of preparing the latter.

The formation of fluorosulphonates by heating mixtures of fluoride and pyrosulphates has been further investigated; the best yields are obtained from potassium pyrosulphate and an excess of ammonium fluoride; the yield is appreciably less when the latter is replaced by potassium fluoride, and still poorer when sodium fluoride is used. Fluorosulphonates are also obtained by heating mixtures of ammonium persulphate with fluoride, or by compressing fluoride and pyrosulphate, particularly in the presence of a little water. H. W.

Reaction of Thiosulphate with Iodine. I. M. Kolthoff (*Pharm. Weekblad*, 1919, **56**, 572—585).—In neutral or weakly acid solution, the reaction between iodine and thiosulphate takes place according to the equation $2Na_2S_2O_3+I_2=Na_2S_4O_6+2NaI$. In weakly alkaline solutions, part of the thiosulphate is oxidised directly to sulphate without the intermediate formation of tetrathionate. The side reaction may be represented in two stages: $I_2+OH'=HOI+I'$, followed by $4HOI+S_2O_3''+6OH'=2SO_4''+4I'+5H_2O$. In sufficiently strongly alkaline solution, all the thiosulphate may in this way be oxidised to sulphate. In strongly acid solution, the reaction is as in neutral solution, the decomposition of the thiosulphate by the acid being slow in comparison with the formation of tetrathionate. W. S. M.

Electrolytic Preparation of Colloidal Selenium. A. Gutbier and G. L. Weise (*Ber.*, 1919, **52**, [*B*], 1374—1378).—When a dilute, aqueous solution of selenium dioxide is electrolysed

between platinum poles (preferably in the presence of a trace of alkali) with a tension of 220 volts, a moderate evolution of gas which does not contain hydrogen selenide is first observed; as soon, however, as the solution attains its boiling point, the formation of colloidal selenium commences, and the solution becomes consecutively yellow, yellowish-red, red, bluish-red, and finally blue. Selenium is not deposited in an irreversible form until the latter stage is reached provided that the original solution is not too concentrated. The yellow systems become yellowish-red when cooled, and can be preserved, even if not dialysed; they can readily be purified by dialysis, are not decomposed by filtration through paper, and can be considerably concentrated by evaporation over a free flame. The yellowish-red solutions sometimes retain their colour and at other times become red when cooled; in the former case, they can be purified by dialysis, and then behave in the same manner as the yellow solutions. The red solutions invariably show a tendency to become bluish-red when cooled—a sign of incipient coagulation; they can only be obtained in a moderately stable condition if dialysed while still hot, and then immediately diluted with pure water or with a solution of a protective colloid, such as gum arabic. The bluish-red and the blue solutions decompose generally when cooled, invariably during dialysis or when preserved at the ordinary temperature. All the dialysed solutions are very sensitive towards electrolytes; red precipitates are thus obtained which pass into the black or grey modification of selenium when heated with the solution of the electrolyte. H. W.

Bibliography of Helium Literature. E. R. Weaver (*J. Ind. Eng. Chem.*, 1919, **11**, 682—688).—A bibliography of the literature connected with helium is given, including everything of scientific interest up to January, 1919. It is classified under the following headings: Discovery and Identification; Occurrence of Helium; Formation of Helium; Separation and Purification; Properties; Liquefaction and Properties of Liquid Helium; Applications of Helium; and Miscellaneous. C. A. M.

The Stability of the Sulphones formed by the Iodides of Sodium, Rubidium, and Cæsium. R. de Forcrand and F. Taboury (*Compt. rend.*, 1919, **169**, 162—165).—The authors have measured the dissociation pressures of the sulphones formed by sodium iodide, rubidium iodide, and cæsium iodide respectively (compare this vol., ii, 341) over a temperature range from $-22{\cdot}5°$ to $20{\cdot}9°$. The three curves practically meet at $-23°$, and at the higher temperatures spread out, the sulphone of sodium iodide having the highest dissociation pressure, that of rubidium iodide the next, that of cæsium iodide being the lowest. At 760 mm., the dissociation temperatures increase with the molecular weight of the sulphone. Calculations of their heats of formation show that these vary in the inverse order. W. G.

The Double Magnesium Potassium Chromate Hexahydrate. A. Duffour (*Compt. rend.*, 1919, **169**, 73—76).—The hexahydrate of the double magnesium potassium chromate, $K_2Mg(CrO_4)_2,6H_2O$, may be obtained if the two chromates are dissolved separately in equimolecular proportions in two and a-half times their weight of warm water, and the solutions are mixed, filtered, and left to evaporate at a temperature not exceeding 15°. After several days, the hexahydrate separates in tabular crystals, which should be removed at once. The crystals may be dried and analysed, but after five or six hours they begin to change slowly into the dihydrate. This dehydration is far more rapid at 120°, but always stops at the dihydrate. The hexahydrate is thus only metastable at even 10°. The crystals are monoclinic [$a:b:c=0{\cdot}7521:1:0{\cdot}4984$; $\beta=103°54'$]. This chromate shows a close analogy to the corresponding sulphate and selenate, and with its rubidium and cæsium analogues forms an eutropic triad. W. G.

Colloidal Cuprous Oxide. Ruoss (*Zeitsch. anal. Chem.*, 1919, **58**, 193—194).—One c.c. of Fehling's solution (copper sulphate 3·5 grams, glycerol 15 c.c., and sodium hydroxide 10 grams per 100 c.c.), 0·5 c.c. of 1% dextrose solution, 1·5 c.c. of urine, and 7 c.c. of water are boiled together and then filtered. The filtrate contains bright red, colloidal cuprous oxide. If 1·5 grams of potassium thiocyanate are added to the 100 c.c. of Fehling's solution, a reagent for the estimation of sugar in urine is obtained. W. P. S.

Adsorption by Colloidal Copper Sulphide. K. Scheringa (*Pharm. Weekblad*, 1918, **55**, 431—435).—A study of the simultaneous precipitation of zinc with the copper sulphide in the separation of copper and zinc. The amount of zinc carried down decreases rapidly with increase in the concentration of acid present and also with rise in temperature for a given acid concentration. The author concludes that the zinc is not adsorbed superficially by the copper sulphide gel, but that at the moment of precipitation a solid solution of zinc in copper sulphide is formed. W. S. M.

The Chemistry of Burgundy Mixtures. Robert Ludwig Mond and Christian Heberlein (T., 1919, **115**, 908—922).

Behaviour of Hydrogen towards Iridium. A. Gutbier, Berta Ottenstein, and G. L. Weise (*Ber.*, 1919, **52**, [*B*], 1366—1368).—The experiments were performed in the same manner as with palladium (Gutbier, Gebhardt, and Ottenstein, A., 1913, ii, 608). The occluded hydrogen is readily expelled by a slight rise in temperature, but removal of the last traces can only be effected by strong heating. The quantity of occluded gas is much smaller than with palladium. The absorption of hydrogen by

iridium with decreasing temperature is at a minimum at about 0°, and with rising temperature is at a maximum at about +20°.

H. W.

Behaviour of Hydrogen towards Platinum. A. Gutbier and O. Maisch (*Ber.*, 1919, **52**, [*B*], 1368—1374. Compare preceding abstract).—The occlusion of hydrogen by platinum black and spongy platinum has been investigated. The former is prepared by adding a boiling solution of chloroplatinic acid neutralised with sodium carbonate to a boiling solution of sodium formate, and is purified by washing with hot water; after being dried in a vacuum over phosphoric oxide or concentrated sulphuric acid, it retains about 0·45% of water and 0·55% of oxygen. Platinum black is converted by dilute hydrochloric acid, and frequently by prolonged boiling of suspensions of it in neutral liquids, into a greyish-black modification, which is reconverted into the black variety by treatment with sodium formate in slightly alkaline solution, or, preferably, with hydrazine hydrate solution. The greyish-black modification appears to represent an intermediate stage between platinum black and spongy platinum.

The following are the chief results of the investigation. Platinum black is far more active towards hydrogen than is spongy platinum; with the latter, the absorption of more than one volume of hydrogen was not observed, whilst with the former as much as 160 volumes were absorbed. The behaviour of platinum black with respect to absorption of hydrogen with increasing temperature is the reverse of that of spongy platinum, with which the amount of gas absorbed increases with rise of temperature. Below 0°, the absorptive capacity of both modifications of platinum diminishes. Platinum black absorbs the maximum quantity of hydrogen at 0°. H. W.

Mineralogical Chemistry.

Ferriferous Sands in Italy. U. Cattaneo and L. Maddalena (*Ann. chim. applicata*, 1919, **11**, 99—108).—Results are given of analyses of ferriferous sands from various parts of the Latium coast, and also of the magnetites separated from such sands. The percentage of Fe_3O_4 in the sand varies from 10·22 to 13·87, and that of TiO_3 from 1·41 to 1·94. The total amount of magnetite present in these sands and others of the Italian coast is calculated to be more than 600,000 tons, 500,000 tons being contained in sand containing more than 5% of magnetite. T. H. P.

Stalactitic Barytes from Madoc, Ontario. T. L. Walker (*Amer. Min.*, 1919, **4**, 79—80).—Curious tubular aggregates of minute, white crystals of barytes occur in veins with fluorspar and

calcite. D 4·29. Analysis shows an unusually large amount of strontium. The peculiar form of the mineral is possibly due to deposition on root fibres.

BaO.	SrO.	CaO.	MgO.	Al_2O_3.	Fe_2O_3.	SO_3.	H_2O.	Total.
43·78	13·95	0·98	1·01	1·92	0·48	36·94	0·26	99·32

L. J. S.

Canadian Minerals [Thaumasite, Saponite, etc.]. R. P. D. Graham (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, IV, 191—201).—Thaumasite occurs as a soft, white coating on joint-planes at the contact of nepheline-syenite and crystalline limestone at Montreal. It forms finely fibrous or loose, mealy aggregates of minute needles. Analysis I agrees with the established formula $3CaO,SiO_2,SO_3,CO_2,15H_2O$; D 1·878. Saponite also occurs at the same locality as a soft, plastic material with much the consistency and appearance of candle grease. On exposure to air, it becomes white and opaque, finally falling to powder, which is soapy to the touch and makes a paste with water. Anal. II, of air-dried material, shows less alumina than is usual in this mineral, and agrees with Clarke's formula, $H_4(MgOH)_2Si_2O_7$. At 40° there is a loss of 8·5%, and since two-thirds of the water is given off below 100°, the formula may be written as an orthodisilicate,

$$H_2Mg_2Si_2O_7,2H_2O.$$

	SiO_2.	SO_3.	CO_2	Al_2O_3.	Fe_2O_3.	FeO.
I.	9·38	13·07	6·71	—	—	—
II.	46·45	—	—	3·32	0·42	0·72

	CaO.	MgO.	H_2O $<100°$	H_2O $>100°$.	Total.
I.	27·32	—	43·69		100·17
II.	—	25·91	14·48	8·13	99·43

Descriptions are also given of phenakite and of a pseudomorph of bismuthinite after molybdenite from pegmatite and quartz veins in granite at Preissac township, northern Quebec, and of albite with new crystal-forms from Ascot mine, Sherbrooke Co., Quebec.

L. J. S.

Manganotantalite from Amelia, Virginia. O. Ivan Lee and Edgar T. Wherry (*Amer. Min.*, 1919, **4**, 80—83).—Crystals of "columbite" occurring in albite at this locality are reddish-brown to black in colour, but in thin splinters ruby-red to orange-brown, and the streak is reddish-brown. D 6·50. H 6—6½. Compared with other members of the columbite-tantalite group, it is seen that there is a slight decrease in the *a*-axis with increasing tantalum content:

	Ta_2O_5. Per cent.	MnO. Per cent.	$a : b : c$.
Standish, Maine.....	9	4	0·4023 : 1 : 0·3580
Haddam, Conn.....	30	5	0·4020 : 1 : 0·3529
Amelia, Va.	53	8	0·4017 : 1 : 0·3562
Sanarka, Russia	80	14	0·4014 : 1 : 0·3505

L. J. S.

Analytical Chemistry.

Device for Guarding against Over-titration. O. Hackl (*Zeitsch. anal. Chem.*, 1919, **58**, 194—198).—A 25 c.c. pipette having practically no stem below its cylindrical bulb and having a length of rubber tubing on its upper stem is placed in the solution to be titrated. The pipette is filled, the tubing closed with a pinchcock, and the titration proceeded with until the solution is slightly over-titrated; the contents of the pipette are then allowed to flow back into the main portion of the solution, and the titration is continued cautiously until the end-point is reached. W. P. S.

The Estimation of Hydrogen Peroxide and the Conservation of Hydrogen Peroxide Solutions. I. M. Kolthoff (*Pharm. Weekblad*, 1919, **56**, 949—959).—Hydrogen peroxide solutions may be conveniently estimated iodometrically. The titration may be carried out directly after the addition of acid and potassium iodide if a few drops of *N*-ammonium molybdate solution are added as a catalyst. For the conservation of peroxide solutions, the addition of 75—100 mg. of acetanilide, benzoic acid, or salicylic acid per litre is recommended. The solution should also react acid to dimethyl-yellow, and should be stored in brown glass bottles. W. S. M.

The Titration of Iodides by means of Conductivity Measurements. I. M. Kolthoff (*Chem. Weekblad*, 1919, **16**, 926—929).—Iodide is completely oxidised to iodine by means of iodate in acid solution according to the equation $5I' + IO_3' + 6H^{\cdot} = 3H_2O + 3I_2$. If the iodide–iodate mixture is titrated with hydrochloric acid and the conductivity measured after each addition of the acid, an approximately constant value is obtained until the oxidation is complete, when a rapid increase in conductivity is observed. The end-point is sharply shown graphically by plotting conductivity against volume of acid added. Iodide may be accurately titrated in this way even in presence of a large excess of bromide, as the analogous oxidation of bromide requires a greater acid concentration and higher temperature. W. S. M.

Precipitation and Filtration of Barium Sulphate in Water Analysis. Victor Froboese (*Chem. Zeit.*, 1919, **43**, 367).—The water is rendered slightly acid with hydrochloric acid, boiled, and treated with a very small excess of barium chloride solution; when cold, the liquid is poured through a filter, the precipitate washed by decantation, and then collected on the filter. W. P. S.

Picramic Acid as a Standard in Colorimetric Estimation of Nitrogen by Nessler's Method. G. Egerer and F. Ford (*J. Lab. and Clin. Med.*, 1919, **4**, 439—442; from *Physiol. Abstr.*, 1919, **4**, 167).—The colour of picramic acid solution is practically

permanent, and the solution serves as a trustworthy standard in the estimation of ammonia by Nessler's method. W. P. S.

A Simplified Macro-Kjeldahl Method for Urine. Otto Folin and L. E. Wright (*J. Biol. Chem.*, 1919, **38**, 461—464).—A method by which an estimation of nitrogen in urine may be carried through in twenty to twenty-five minutes. The urine (5 c.c.) is boiled over a micro-burner with 5 c.c. of a mixture of sulphuric and phosphoric acids containing copper sulphate and 2 c.c. of 10% ferric chloride solution. Oxidation should be complete in about eight minutes, whilst the distillation may be carried through in five. Urines containing much sugar require oxidation with fuming sulphuric acid. J. C. D.

Estimation of Ammonia in Blood. Sergius Morgulis and H. M. Jahr (*J. Biol. Chem.*, 1919, **38**, 435—438).—The aeration method for determining ammonia in blood is open to many inaccuracies. The authors propose to remove protein from the blood before carrying out the estimation. This they do by means of metaphosphoric acid. Ammonia in the protein-free filtrate is adsorbed by permutite, from which it is again liberated by sodium hydroxide and determined colorimetrically by the Nessler process. J. C. D.

Method for the Estimation of Nitrates in Water by means of the Phenolsulphonic Acid Reaction. Robert C. Frederick (*Analyst*, 1919, **44**, 281—284).—The presence of large quantities of chlorides (up to 100 parts of chlorine per 100,000 parts of water) does not interfere with the estimation of nitrates by the phenolsulphonic acid method if the water (25 c.c.) is evaporated with 2 c.c. of reagent containing 4 grams of phenol and 400 c.c. of sulphuric acid per litre. The evaporation should be carried as far as possible on a water-bath, the residue then dissolved in water, again evaporated, dissolved in 95 c.c. of water, the solution treated with 3 c.c. of concentrated ammonia, diluted to 100 c.c., and the coloration obtained compared with that produced by a known amount of nitrate under similar conditions. W. P. S.

Estimation of Carbon in Soils by the Wet Combustion Method. D. D. Waynick (*J. Ind. Eng. Chem.*, 1919, **11**, 634—637).—In estimating carbon in soils and the like by Ames and Gaither's method of wet combustion (*J. Ind. Eng. Chem.*, 1915, **7**, 561), Gortner weighed the carbon dioxide after absorption in potassium hydroxide, whilst Schollenberger (A., 1916, ii, 395) used barium hydroxide as an absorbent and titrated the excess of alkali with acid. The drawback to the first method is the time required for the absorption, and to the second the difficulty of preventing the barium hydroxide absorbing carbon dioxide from the air. These drawbacks are obviated in a simple modification of the method, in which the carbon dioxide is absorbed in a soda-lime absorption bulb and estimated gravimetrically. A

complete estimation may be made in twenty-five minutes. [See also *J. Soc. Chem. Ind.*, 1919, 591A.] C. A. M.

Estimation of Carbon Disulphide. A Critical Examination of the various Methods usually Employed. PERCY E. SPIELMANN and F. BUTLER JONES (*J. Soc. Chem. Ind.*, 1919, **38**, 185—187T).—Determination of the specific gravity of benzene before and after extraction of carbon disulphide with alcoholic potassium hydroxide solution gives a fairly accurate measure of the quantity of carbon disulphide present, the error being within 0·03%. Oxidation of the above alkaline extract with bromine and estimation of the resulting sulphate are also trustworthy. Volumetric or gravimetric estimation of the xanthate in the alkaline extract, by titration or precipitation with copper sulphate solution, was found to be untrustworthy, as was also a method depending on the precipitation of carbon disulphide with phenylhydrazine. Precipitation of the xanthate with lead acetate did not yield good results. W. P. S.

Electrolytic Separation of Lead from Chromium and Analysis of Chrome Yellow and Similar Pigments. JAROSLAV MILBAUER and IVAN ŠETLÍK (*J. pr. Chem.*, 1919, [ii], **99**, 85—92).—According to Vortmann (A., 1907, ii, 302), the electrolytic separation of lead peroxide in presence of sulphuric, selenic, or chromic acid leads to high results, it being necessary to redissolve the peroxide and repeat the separation. Smith ("Electrochemical Analysis," 3rd ed., 1907, 165), however, states that lead may be separated accurately as peroxide from the alkali and alkaline earth elements, glucinum, magnesium, mercury, and aluminium, and that the presence of chromic acid is without influence on the quantitative separation. The authors find that $Pb^{\cdot\cdot}$ may be easily separated electrolytically from $Cr^{\cdot\cdot\cdot}$ if 150 c.c. of the electrolytic solution contains 0·2 gram of lead, 0·1 gram of chromium, and 20 c.c. of nitric acid (D 1·4), and that addition of 15 c.c. of perchloric acid (D 1·12) does not invalidate the results. This method is applicable to the analysis of pigments with a basis of lead chromate, the pigment being dissolved in nitric and perchloric acids and the diluted solution electrolysed; the chromium is afterwards precipitated as hydroxide and weighed as Cr_2O_3. [See also *J. Soc. Chem. Ind.*, 1919, September.) T. H. P.

Estimation of Minute Amounts of Lead in Urine, Fæces, and Tissues. W. DENIS and A. S. MINOT (*J. Biol. Chem.*, 1919, **38**, 449—452).—The evaporated urine (2000 c.c.) or the dried tissue or fæces (500 grams) is oxidised with sodium nitrate in a silica vessel. After the oxidation, the vessel is cooled and the contents treated with 10% hydrochloric acid until the reaction is faintly acid. The mixture is heated to boiling, filtered while hot, and made faintly alkaline with ammonium hydroxide. Two or three drops of a 1% solution of copper sulphate are then added, and

the copper and any lead precipitated by the addition of hydrogen or ammonium sulphide. The suspension of sulphides is separated by centrifugalisation, and washed very carefully in order to remove magnesium, phosphates, and chlorides.

The final residue of sulphides is transferred to a platinum crucible of 25 c.c. capacity by means of 3 c.c. of dilute nitric acid (20 parts of concentrated acid, D 1·42, and 80 parts of water), and the centrifuge tube washed out with 3 c.c. of distilled water. The solution is then electrolysed with a current of 3 to 3·5 amperes and 5 to 6 volts, the crucible serving as anode and a spiral of platinum wire as cathode. Within fifteen minutes, all the lead is deposited on the crucible anode in the form of a brown film of lead peroxide, whilst the copper and any traces of iron are deposited on the cathode. Care must be taken not to cut off the current while the lead peroxide is in contact with nitric acid, so that it is necessary to remove the acid by siphon while the electrolysis is proceeding, replacing it at the same time by distilled water. The crucible is washed, and 5 c.c. of a 5% solution of potassium iodide (free from iodate) and 1 c.c. of 25% acetic acid are added. The lead peroxide decomposes, giving a yellow deposit of lead iodide on the crucible and a solution of free iodine. After five minutes, the liquid is transferred to a small beaker and titrated with 0·005*N*-sodium thiosulphate solution. J. C. D.

Apparatus for Measuring the Volume of Gas Evolved during a Chemical Reaction. P. Nicolardot and M. H. Robert (*Chim. et Ind.*, 1919, **2**, 641—646).—A modification of an apparatus described previously by one of the authors (A., 1912, ii, 597), particularly designed for measuring the volume of hydrogen liberated when aluminium is dissolved in sodium hydroxide solution. The reaction vessel consists of a tube which is connected with a reflux apparatus, and this in turn with the measuring burette. The latter is filled with water and is surrounded by a water-jacket. A diagram of the apparatus is given in the original and the method of using it is explained in detail. W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. L. Brandt (*Chem. Zeit.*, 1919, **43**, 373—374).—The use of colloidal silica as recommended by Schwarz and Rolfes (this vol., ii, 170) to prevent the action of hydrochloric acid on permanganate in the titration of ferrous salts is untrustworthy. It is shown that the larger the quantity of silica added, the less permanganate is required for the titration. This occurs in both hydrochloric and sulphuric acid solutions. W. P. S.

Rapid Method for Estimating Nickel and Cobalt in Ores and Alloys. III. W. R. Schoeller and A. R. Powell (*Analyst*, 1919, **44**, 275—280. Compare A., 1917, ii, 425).—Further work on the method described previously showed that modification is necessary when the material contains manganese or certain other

elements; the addition of solid potassium iodide instead of saturated sodium chloride solution to the ammoniacal tartrate solution promotes complete precipitation of the cobalt as hexaminecobaltous iodide in the case of ores containing little or no nickel. The following is a summary of the procedure recommended for the analysis of ores.

(1) The ore is free from copper, manganese, calcium, and magnesium; presence of arsenic immaterial. The sample is dissolved in nitric acid, the solution evaporated almost to dryness, and tartaric acid (ten times the weight of tervalent metals present) dissolved in water is added. The mixture is then treated with 50 c.c. of concentrated ammonia and 3 to 5 grams of potassium iodide, and, after fifteen minutes, the precipitate is collected, washed with ammoniacal potassium iodide solution, and dissolved in dilute hydrochloric acid. The solution is filtered, the cobalt precipitated as phosphate, and the nickel titrated in the filtrate from the latter precipitate.

(2) The ore contains copper, otherwise the same as (1). The method is the same as that above up to the point where the iodide precipitate is dissolved in hydrochloric acid. The solution is decolorised by the addition of sulphurous acid, boiled, cooled, filtered to separate cuprous iodide, etc., and the cobalt then precipitated as phosphate.

(3) General procedure for ores free from manganese. The acid solution of the ore is treated with hydrogen sulphide, filtered, the filtrate treated with ammonium chloride and a slight excess of ammonia, and saturated with hydrogen sulphide. The precipitate obtained is dissolved in aqua regia, and the solution is evaporated almost to dryness, etc., as described under (1).

(4) The ore contains manganese. If only small amounts of manganese are present, the ammonium cobalt phosphate precipitate may be titrated with $N/5$-acid (not hydrochloric acid), or the weighed cobalt pyrophosphate precipitate may be dissolved in sulphuric acid and the amount of manganese estimated by the persulphate–silver nitrate method. For large amounts of manganese, the mixed iodide precipitate is dissolved in dilute acid, and the nickel and cobalt precipitated as sulphides from an acetic acid solution, or the acid solution may be neutralised and the cobalt and nickel precipitated as xanthates. In the case of nickel ores free from cobalt, manganese does not interfere with the cyanide titration in the presence of citrate. W. P. S.

Estimation of Urea. PHILIBERT (*J. Pharm. Chim.*, 1919, [vii], **19**, 335—346, 386—397, 434—441).—A method which is more trustworthy than those described by Folin and by Fosse (A., 1917, ii, 73), particularly in the case of urine containing sugar, consists in treating 10 c.c. of the urine with 2 c.c. of basic lead acetate solution, diluting the mixture to 50 c.c., and filtering. Ten c.c. of the filtrate are treated with 5 c.c. of 10% sodium hydroxide solution in the ureometer, a definite volume of hypobromite is

added, and the mixture shaken so as to mix it thoroughly with the mercury contained in the apparatus. The gas evolved is measured under the usual conditions. A control experiment is made, using a standard urea solution and the same quantities of reagents as in the first experiment. Allowance is made for any ammonia present, this being estimated separately. W. P. S.

Ureometer with a Reaction Bulb of Variable Capacity. Boyer (*J. Pharm. Chim.*, 1919, [vii], **19**, 346—349).—The apparatus consists of a wide tube constricted at its lower end so as to form a graduated tube; the wide tube is divided into two parts, which are connected by a rubber tube which keeps the two ends a short distance apart. Hypobromite solution and water are introduced into the apparatus so as to fill the graduated portion, a glass ball is then placed in the apparatus, thus closing the top of the graduated tube, and the solution in which the urea is to be estimated is added. The two wide tubes are now pressed together, thus folding the rubber connexion in pleats, the whole apparatus is filled with water, closed with a rubber stopper, and inverted. The contents mix, the volume of the gas liberated being accommodated by the rubber connexion; the total volume of the gas is determined in the usual way. W. P. S.

A Reaction for Lecithin. H. J. Hamburger (*Arch. Néerland. physiol.*, 1919, **3**, 361—364).—This test will detect 0·01% of lecithin present in fluids containing proteins. The proteins are removed by adding three volumes of 96% alcohol and filtering or centrifugalising. On the addition of dilute sulphuric acid (1:5) to the clear filtrate, a cloudy precipitate of lecithin is formed, which dissolves on warming and reappears on cooling. J. C. D.

Detection and Estimation of Cocaine, Heroine, and Veronal in Viscera. P. A. Ellis Richards (*Analyst*, 1919, **44**, 192—196).—A weighed portion of the viscera is acidified with acetic acid and extracted with warm alcohol; the alcoholic solution is concentrated, filtered, clarified with lead acetate, and the excess of lead removed as sulphide, again concentrated, acidified with acetic acid, and extracted with ether. The ethereal extract is evaporated, the residue dried, weighed, and examined for veronal, trional, sulphonal, etc. The aqueous solution, after the extraction with ether, is rendered ammoniacal, extracted with chloroform, the chloroform solution shaken with dilute hydrochloric acid, this acid extract again rendered ammoniacal, extracted with chloroform, and the residue, if any, obtained after evaporating the chloroform, is extracted with benzene, in which cocaine is distinctly soluble. For the examination of the urine, the sample is acidified with acetic acid, boiled, clarified with lead acetate, and then treated as in the case of viscera. The final residues are then submitted to special tests for their identification.

Notes are given on tests for certain narcotics. [See, further, *J. Soc. Chem. Ind.*, 1919, 512A.] W. P. S.

The Metabolism of Bile Acids. I. A Quantitative Method for Analysis of Bile Acids in Dog's Bile. (Miss) M. G. Foster and C. W. Hooper (*J. Biol. Chem.*, 1919, **38**, 355—366).—Dog's bile contains taurocholic and taurocholeic acids, which, on hydrolysis, yield cholic and choleic acids and taurine. Taurine reacts quantitatively with nitrous acid under the conditions employed in the Van Slyke apparatus, and this fact is made the basis for the analytical procedure. Five c.c. of bile cleared in a centrifuge are precipitated with 40 c.c. of 96% alcohol, and heated to boiling point to ensure complete solution of the acids. After cooling, the mixture is made up to 50 c.c. with 95% alcohol and passed through a dry filter. Two portions of 20 c.c. are evaporated to dryness. One is washed out with water and made up to 10 c.c. in a volumetric flask. Samples of 2 c.c. of this are used to determine the nitrogen present in amino-form before hydrolysis. The other sample is hydrolysed by being heated on the water-bath for five hours with 6 c.c. of 8% sodium hydroxide. This sample is made up to 10 c.c. and the amino-nitrogen again determined in 2 c.c. portions. The difference represents the nitrogen present in the amino-group of taurine. For conversion of the nitrogen figure into one representing taurocholic acid, the factor 36·72 is used. J. C. D.

An Electrical Method of Determining the Lime Requirement of Soils. C. J. Lynde (*Trans. Roy. Soc. Canada*, 1918, [iii], **12**, III, 21—26).—Two lots of 10 grams each of soil are shaken respectively with 150 c.c. of distilled water and 150 c.c. of a solution of calcium hydrogen carbonate for three hours, as in the Hutchinson and MacLennan method (compare A., 1914, ii, 784). The electrical resistance of the aqueous soil solution and of the calcium hydrogen carbonate solution before and after shaking with the soil is determined. If these are represented by r_1, r_2, and OR respectively, then the value of r, the calculated resistance of the calcium hydrogen carbonate solution after being shaken with the soil and allowing for the resistance of the aqueous soil solution, is given by $r = r_1 \times OR/(r_1 - OR)$. Then the ratio r/r_2 should give a measure of the alkalinity or acidity of the soil. Comparing these results with those obtained by the Hutchinson and MacLennan method (*loc. cit.*), it is found that if the ratio is less than 0·986, the soils are alkaline, whilst if the ratio is above 1·284, the soils are acid and require liming. W. G.

General and Physical Chemistry.

Index of Refraction and Molecular Refraction of Aqueous Solutions of Nicotine. Augusto Levi (*Atti R. Ist. Veneto Sci.*, 1915, **75**, 465—479).—Measurements were made by the method of minimum deviation on a good spectrometer. The temperature was not constant, but was kept sufficiently near 24°. Sixteen concentrations were used. Pulfrich's method of calculation is: $P[(n-1)/d][(1-\alpha C)/(1-C)] = P_1[(n_1-1)/d_1] + P_2[(n_2-1)/d_2]$. P, P_1, P_2 are the weights, n, n_1, n_2 the refractive indices, and d, d_1, d_2 the densities, respectively, of the mixture and of the two components. C is the coefficient of contraction, and equals $(d-d_0)/d$, in which d_0 is the density the mixture would have if no contraction took place on mixing, and α is a constant derived from the empirical relation $(d-d_0)/d = \alpha[(n-1)-(n-1)_0]/(n-1)$, in which $(n-1)_0$ is the value $n-1$ would have if no contraction took place. This gave results more consistent with experimental data, and indicated that methods of calculation based on the hypothesis that the n of mixtures is additive are not accurate. The molecular fraction for water (q_a) and nicotine (q_b) was calculated by the method of Schulze. $q_a+q_b=1$; $q_a=(p_a/m_a)/[(p_a/m_a)+(1-p_a)/m_b]$; $q_b=(1-p_a/m_b)/[(p_a/m_a)+(1-p_a)/m_b]$; the experimental molecular refraction calculated from the rule of mixtures, according to the Dolezalek-Schulze theory, shows that the water and nicotine form solutions without dissociation phenomena.

Chemical Abstracts.

Optical Activity. I. Temperature-rotation Curves for the Tartrates at Low Temperatures. T. S. Patterson and K. L. Moudgill (*Proc. Roy. Soc. Edin.*, 1919, **39**, 18—34).—Rotation–temperature curves have been produced from measurements of the rotation of ethyl *d*-tartrate and *iso*butyl dibenzoyl-*d*-tartrate dissolved in cinnamaldehyde and ethylene dibromide respectively at a series of temperatures from 0—181° in the first-named solvent and 17·7° and 39·7° in the last-named solvent. A consideration of the present results and previously published results (T., 1908, **93**, 1844; 1912, **101**, 378; 1913, **103**, 152; 1916, **109**, 1145) shows that a general temperature–rotation curve may be produced for all tartrates. J. F. S.

Value of the Silver Oun. W. M. Hicks (*Phil. Mag.*, 1919, [vi], **38**, 301—317. Compare A., 1913, ii, 810).—A theoretical paper in which an attempt is made to calculate the value of the oun for silver to an accuracy of 1 per 100,000. In general, it is shown that $q=361{\cdot}7837+0{\cdot}001628dN\pm0{\cdot}0038$, for silver $\delta=421{\cdot}0470+0{\cdot}001894dN\pm0{\cdot}0045$. If the atomic weights in terms of the silver value are determined from the oun, the values are independent of the actual N used, provided it can be taken as the same for all elements. They should be calculated, therefore, either

with $N=109675$ if in *R.A.* or 109678·6 if in *I.A.* and the value $q=361{\cdot}7837\pm0{\cdot}0038$ used. J. F. S.

Series Spectra according to the Bohr Atom Model. Franz Tank (*Ann. Physik*, 1919, [iv], **59**, 293—331).—A mathematical paper in which relationships of the series spectra are deduced on the basis of Bohr's conception of the atom. These relationships are examined in connexion with the series spectra of hydrogen, helium, parhelium, and lithium. J. F. S.

Principle of Choice and the Displacement Law for Series Spectra. W. Kossel and A. Sommerfeld (*Ber. Deut. physikal. Ges.*, 1919, **21**, 240—259).—A theoretical paper in which the co-ordination of spectrum lines into series on the basis of the quantum theory is discussed. It is shown that the series of doublets of the alkaline earths are spark spectra; their character as a system of doublets explains itself from the doublet character of the arc spectrum of the alkalis. A simple numerical relationship exists between the spark spectrum of the alkaline earths and the arc spectrum of the next preceding alkali metal. J. F. S.

Effect of an Electric Field on the Pressure Displacement and the Broadening of Series Lines. M. Ritter (*Ann. Physik*, 1919, [iv], **59**, 170—184).—The effect of an electric field of approximately 26,000 volt/cm. on the series lines of zinc, mercury, lithium, and calcium is to cause the pressure displacement and the unsymmetrical broadening to increase along a series with increasing member number, and also with decreasing wave-length. The sign of the displacement by an electric field is always the same as the sign of the displacement by increase of pressure and the sign of the dissymmetry. These results confirm experimentally Stark's hypothesis that the pressure displacement and the unsymmetrical broadening is brought about by an intra-molecular electric field. J. F. S.

Structure of the Band Spectra of Burning Hydrocarbons. T. Heurlinger and E. Hulthén (*Zeitsch. wiss. Photochem.*, 1919, **18**, 241—248).—The band spectrum of an acetylene flame has been photographed in the first three orders by means of a concave grating 6·4 m. diameter ruled 400 lines per cm. The bands in general can be represented by three whole numbers, m, n, p, and a second class of bands in which the n, p, values correspond with a system of six series, P_i, Q_i, and R_i ($i=1, 2$). The lines of these six series are given in the paper and the relationships between them worked out. J. F. S.

Effect of an Electric Field on the Spectrum Lines of Argon. Toshio Takamine and Noboru Kokubu (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 281—285).—The Stark effect on the argon spectrum lines has been examined, using a field of 170,000 volt/cm., by Lo Surdo's method. The lines λλ 4933·5, 4510·9, 4335·4, 4333·7, 4300·2, 4272·3, 4259·5, 4200·8, 4198·4, 4191·0, 4182·0, 4164·4, 4158·7, 4153·0, 4132·0, 4046·0 Å. are all slightly displaced toward the red.

Practically all the lines affected by an electric field belong to the red spectrum of argon, and the so-called arc lines seem to be more easily affected than the spark lines. This is in keeping with the results obtained in the case of helium, calcium, and magnesium. The mercury line λ 4339 Å. was found to be displaced about 0·7 Å. for the *p*-component and 0·5 Å. for the *s*-component toward the red end in a field of 53,000 volt/cm. J. F. S.

Effect of an Electric Field on the Spectrum Lines of Helium. III. Toshio Takamine and Noboru Kokubu (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 275—280. Compare A., 1918, ii, 253).—The effect of an electric field on the spectrum lines of helium has been continued with the lines λλ 4009, 3889, 3868, 3830, 3448, 3188, and 2945 Å.; these lines are examined for the first time. The lines λλ 4438, 4121, and 3965 Å., which have previously been stated to be slightly displaced by an electric field, are found to be resolved into a number of components all of which are displaced in the same direction. A striking similarity is noted between the Stark effect on the helium lines λλ 4388 and 4026 Å. and the Hγ line in the fact that the central line in the *s*-component is the strongest of all the components, and it is displaced toward the red as the field strength is increased. In the present work an echelon grating was used for examining the Stark effect, and the advantages of this arrangement are discussed. The faint line accompanying λλ 5876 and 4472 Å. has been examined in this way. Numerous diagrams and photographs are appended to the paper. J. F. S.

Effect of an Electric Field on the Spectrum Lines of Hydrogen. II. Toshio Takamine and Noboru Kokubu (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 271—273. Compare A., 1917, ii, 401).—Experiments previously described have been repeated with slight modifications; a tantalum cathode was used instead of an aluminium one, and the pressure in the tube was further reduced, so that it was possible to obtain a field strength of 150,000 volt/cm. It is shown that the central line in the perpendicular component of H_γ is shifted about +1 Å. at a field of 130,000 volts/cm. In the case of the H_α line six *p*-components and three *s*-components were observed, a fact in keeping with the later work of Stark (*Ann. Phys.*, 1915, **48**, 183). In the secondary hydrogen spectrum the authors have noted a further eleven lines in the region below λ 4000 Å. which are affected by an electric field. J. F. S.

Spectrum Lines of Oxygen and Nitrogen in an Intense Electric Field. Usaburo Yoshida (*Mem. Coll. Sci. Kyoto*, 1919, **3**, 287—297).—The Stark effect on the spectrum lines of oxygen and nitrogen has been examined in fields up to $16{\cdot}5 \times 10^4$ volt/cm. and a positive result observed with the lines λλ 4100 and 4110 Å. of nitrogen and with some of the lines belonging to the first and second subordinate triplet series of oxygen. Excepting a few ambiguous cases, the amount of displacement or of separation of each of these lines is nearly equal respectively in both the parallel and

perpendicular components. The behaviour of the lines of the second subordinate triplet series of oxygen in the electric field is similar to that of the lines belonging to the second subordinate series of helium and parhelium. The effect on the spectrum lines of the first subordinate triplet series of oxygen is larger than that on the second subordinate triplet series. Each of the lines λλ 5329·5 and 4968·5 Å. of the first subordinate triplet series has two isolated components respectively in its immediate violet side. The isolation of the said components becomes smaller as the term number of the series increases. This is exactly similar to that of the isolated components of helium and parhelium. Diagrams and photographs of the resolved lines are appended to the paper.

J. F. S.

Lithium Spectrum in an Electric Field. Usaburo Yoshida (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 161—171).—The effect of an electric field of 30,000 volt/cm. on the lithium lines λλ 6103·8, 4602·4, 4132·4, and 4148·2 has been determined by Lo Surdo's method. The line λ 6103·8 is unaffected by the field employed. In the case of the line λ 4602 two vertical and two parallel components only were observed; the central component observed by Stark did not appear. The separation of the parallel components is somewhat greater than that of the perpendicular components. The intensity of the violet component is less than that of the red component. The line λ 4132 is separated into three components, the displacement of the parallel components being somewhat smaller than those of the perpendicular components. The helium lines have been compared with the lithium lines under the same conditions of treatment. The peculiarity of the lines λλ 4602 and 4148·2 in the arc has been explained as due to the effect of an electric field on these lines. Photographs of the separated lines are appended to the paper.

J. F. S.

Effect of an Electric Field on the Spectrum Lines of Calcium and Magnesium. Toshio Takamine and Noboru Kokubu (*Mem. Coll. Sci. Kyoto*, 1918, **3**, 173—181).—Making use of Lo Surdo's method, the effect of an electric field on the calcium and magnesium lines has been investigated. Quantitative measurements have been made with the calcium lines λλ 4685, 4355, 4099, 4095, 4093, 3645, and 3631 Å. and with the magnesium lines λλ 4352, 3097, and 3093 Å. The maximum electric field employed was 90,000 volt/cm. The above-mentioned lines and others between λλ 5042 and 3624 Å. which were not measured were all displaced in one direction or the other in the electric field. In general, the lines belonging to the same series were affected in nearly the same way, and, further, each line constituting a triplet was affected in the same way. The latter is well shown in the case of the lines λλ 4099, 4095, and 4093 Å. belonging to the narrow triplet series. The magnesium triplet λλ 3838, 3833, and 3830 Å. seems to be an exceptional case, but as the lines are only very slightly affected, further experiments, using a larger dispersion, are

needed for confirmation. Photographs of the displaced lines are appended to the paper. J. F. S.

The Arc Spectrum of Dysprosium. Josef Maria Eder (*Sitzungsber. K. Akad. Wiss. Wien*, 1918, II A, **127**, 1100—1228; from *Chem. Zentr.*, 1919, i, 914. Compare A., 1918, ii, 181).—It appears possible on spectroscopic evidence that an unknown element, closely related to terbium, is present in the terbium–dysprosium fractions, the spectrum of which is mixed with that of the actual terbium and dysprosium. To obtain further insight into this probability, the author has examined the arc spectrum of pure dysprosium over its whole length. The specimen used was supplied by Auer von Welsbach. The sulphate was converted into the chloride since the latter salts of the rare earths give more powerful arc spectra with less prominence of carbon bands than do the oxides or sulphates. The colour of the arc flame was pale green, but not nearly so intense as with cassiopeium and aldebaranium. The wave-length table given by the author contains 4385 lines, including many new ones in the red, yellow, and extreme ultra-violet regions. No definite evidence of fission of dysprosium is obtained, so that it may be regarded as a well-defined element which can be isolated in the pure condition by various processes of separation, and through the spectrum of which further information may be obtained with respect to the yet uncertain terbium. The lines of the dysprosium arc spectrum are generally sharp, and only broaden slightly after protracted illumination; in addition, a more or less well-defined band spectrum is shown in the visible portion. The first of these bands has its main edge at 5693 Å.U. The second, broadened band has its brightest edge at 5404; the main edge of the third, well-defined band lies at 5263. Contrary to the views of Eberhard, the lines of dysprosium are not generally present in the spectrum of the sun, in which the presence of this element cannot be detected. H. W.

Is the Absorption [of Light] (Vierordt) a Characteristic Value, Independent of the Apparatus (Spectrophotometer) Employed? Paul Hári (*Biochem. Zeitsch.*, 1919, **95**, 266—271).—The values are characteristic, and are not influenced by the type of apparatus, provided the construction and calibration of the instrument are satisfactory. J. C. D.

Absorption Spectra of Aqueous Solutions of Colourless Metallic Complex Salts. Yuji Shibata, Kurazo Fukagawa, and Jun Asado (*J. Tokyo Chem. Soc.*, 1919, **40**, 311—338).—The following solutions were used: $[Pt(NH_3)_4]Cl_2$; $[Ag(NH_3)_2]Cl$; $[Ag_2(NH_3)_2]SO_4$; $[Ag(NH_3)_2]NO_3$; $\left[Cu\left(CS<\begin{matrix}NH_2\\NH_2\end{matrix}\right)_3\right]Cl$; $[Zn(NH_3)_4]Cl_2$; $[Zn(NH_3)_4]I_2$; $[Zn(NH_3)_5]SO_4$; $Zn_3AsO_4,2NH_3,3H_2O$; $\left[Zn\left(CO<\begin{matrix}NH_2\\NH_2\end{matrix}\right)_2\right]Cl_2$;

$[Sn(NH_3)_2]Cl_4$; $[Cd(NH_3)_2]Cl_2$; $\left[Cd\left(CO<\begin{matrix}NH_2\\NH_2\end{matrix}\right)_2\right]Cl_2$;
$[Al(NH_3)_6]Cl_3$; $[Fe(CN)_6]K_4$; $[Co(CN)_6]K_3$; $[Co(CN)_6]Ag_3$;
$CuCN,2KCN,KSCN,\frac{1}{2}H_2O$;
$3AgCN,2KCN,NaCN$; $AgCN,KCN$; $2Hg(CN)_2,Mg(SCN)_2$;
$2Hg(CN)_2,Ba(SCN)_2$; $Hg(CN)_2,AgNO_3,2H_2O$;
$Hg(CN)_2,K_2S_2O_3,H_2O$;
$2Hg(CN)_2,3CuCN,KCN,KSCN$; $2Hg(CN)_2,KOH,H_2O$;
$Hg(CN)_2,KSCN,2KCN,\frac{1}{2}H_2O$;
$3Hg(CN)_2,[Fe(CN)_6]K_4,H_2O$; $Hg(CN)_2,HgO$. The results are given in sixteen curves; the logarithms of the thickness of the layers are plotted against wave-lengths at the limits of absorption. Aqueous solutions of colourless metallic complex salts absorb the light more than those of their simple metallic salts, showing that the formation of the complex ions is responsible for the phenomenon. In general, ammonia complexes are more strongly absorbent than cyanogen complexes. The absorbing power of complex silver salts is no greater than that of simple silver salts, probably due to the fact that $Ag^{\cdot}$ of the simple salts already exists as a complex form of Ag_2'' (compare M. Traube, A., 1886, 661). Cadmium and aluminium complexes are equally as transparent as their corresponding simple salts, as far as the ultra-violet zone is concerned (their plates were sensitive to only $\lambda=2000$); a hypothesis is given for this peculiarity. All complex salts (except those containing cobalt) give only end absorptions, but not absorption bands; occurrence of the selective absorption depends on the characteristic of metals in the complex. Those complexes containing SCN groups produce selective absorptions, regardless of the kind of metals they contain. In complexes having similar structures, the metals which have greater atomic volumes possess less absorptive power than those having smaller atomic volumes. In complexes containing the same metals, even if their structures may be unknown, it is true that the more components the salt has and the more complex it is, the stronger will be the power of absorption.

CHEMICAL ABSTRACTS.

Ultraviolet Absorption of Pyridine, α-Picoline, β-Picoline, and Piperidine. ERNST HERRMANN (*Zeitsch. wiss. Photochem.*, 1919, **18**, 253—278).—The absorption spectra of pyridine, α-picoline, β-picoline, and piperidine have been measured in the region λλ 2696—3017 for both vapour and alcoholic solutions. For the vapours of pyridine, α-picoline, and piperidine previous measurements were repeated; in the case of β-picoline the ultra-violet absorption is represented by three broad bands. Series, similar to those observed for benzene derivatives, are evolved. In the α-picoline spectrum a series of similar structure to one of the pyridine series is observed. In the case of piperidine a structure is observed which is similar to that observed for benzene and is characterised by the appearance of series which may be resolved into typical groups. The spectra obtained from capillary layers of the liquids

and from alcoholic solutions (1 gram-mol. in 20, 100, and 500 c.c. of alcohol) are made up of ill-defined bands. J. F. S.

Influence of Different Substances on the Absorption of Light by Thin Tungsten Layers. L. Hamburger, G. Holst, D. Lely, and E. Oosterhuis (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1078—1088).—The present paper describes experiments designed to increase the life of tungsten lamps by removal of the tungsten layer produced on the walls of the lamp as it burns. Two classes of substances come under consideration: (i) gases which form less coloured compounds with the tungsten sublimate, and materials which produce these gases; (ii) substances which decolorise the tungsten layer in some way which is probably not chemical. The first group of substances includes chlorine and substances, such as K_3TlCl_6, which evolve chlorine on heating. This class of substance is reviewed. Experimental work with the second group of substances is described. The light absorption of the tungsten sublimate is decreased when previous to burning the filament is coated with a layer of sodium chloride, sodium phosphate, potassium cyanide, sodium oxide, sodium fluoride, or calcium fluoride. On passing the current through the lamp these substances sublime and are condensed in a non-crystalline condition on the wall of the lamp, and have the effect of increasing the life of the lamp. The action of these substances is not understood, but a discussion is entered into in the paper on the subject. If the deposit is rendered crystalline by the admission of moist air it loses its efficacy. The life of a lamp using sodium chloride is increased 2·6 times, and of one using calcium fluoride 3·3 times. J. F. S.

A New Photographic Phenomenon. Donald Neil McArthur and Alfred Walter Stewart (T., 1919, **115**, 973—974).

The Secondary Radiation Produced by α-Rays. B. Bianu (*Le Radium*, 1919, **11**, 230—234. Compare A., 1913, ii, 371).—By means of an apparatus described, the existence of an ionising radiation (δ-rays), produced by impact of α-rays on glass and metal surfaces, has been clearly put in evidence and the characteristics of the radiation studied. α-Rays from a polonium surface strike a plate, and the ionisation at various gas pressures produced by secondary radiation from the plate is measured in an ionisation chamber below, the upper surface of which is of wire gauze. The ions produced by the α-rays are prevented from reaching the ionisation chamber by a suitable electric field. The secondary radiation consists of (1) a small part of the α-rays reflected, (2) a secondary radiation of the β-type, of velocity 3×10^9 cm./sec., which corresponds with a generating potential of 2400 volts; (3) an electronic radiation of feeble velocity (δ-rays), completely absorbed by 0·5 μ of aluminium, and ionising the air over a very limited range, given by $pa = 110$, where p is the pressure and a is the range, both in mm. The number of electrons in (3) is about forty times the number of (2) and about ten times the number of reflected α-particles. It does not differ greatly with the character of the surface

struck by α-rays, whether it be of glass or of various metals. Probably these electrons are all emitted with the same velocity, corresponding with about 20 volts, but suffer partial absorption in a very thin film of the generating surface before escaping, so that their actual velocity varies from that corresponding with from 0 to 20 volts. F. S.

The Question of the Existence of Isotopes with the same Atomic Weight. The End Products of the Thorium Disintegration Series. STEFAN MEYER (*Monatsh.*, 1919, **40**, 1—14) —The radiation from a specimen of lead, separated by Soddy from Ceylon thorite of atomic weight 207·77, has been examined to test the view whether one of the two isotopes of lead of the same atomic weight, produced as the ultimate products by the branching of the disintegration series, undergoes further change with emission of radiation as yet undetected. The α-radiation from the lead was found exactly to correspond in intensity with what is to be expected from the polonium regenerated from radium-*D*, which is necessarily present in this lead, being derived from the small amount of uranium in the original mineral. From a solution of the chloride in water, the polonium was separated by electrolysis on a gold cathode, using a platinum anode, and the range and character of its α-rays were found to be identical with those of a preparation similarly separated from Joachimsthal pitchblende. The discrepancy between the atomic weight of this lead, 207·77, and what it should be, 208·0, if both end-products are stable, must be explained otherwise than by supposing one of the products to be unstable. There must be 26% of common lead present to account for the difference, or Lawson's hypothesis (*Sitzungsber. K. Akad. Wiss. Wien*, 1917, **126**, 723) that there may be a gradual replacement of thorium by uranium in thorium minerals in the earth may be the explanation. There is also no evidence as to what becomes of the product, supposed to be unstable, derived from the composition of thorium minerals. It is known not to change into mercury or bismuth, and the existence of any large quantity of an isotope of polonium in thorium minerals is also excluded by the evidence. As regards thallium, Exner and Haschek have found considerable quantities by the spectroscope in Cornish pitchblende, but Hoernes, in a careful analysis of 1 kilogram of thorium-rich, but uranium-poor, monazite could not detect thallium, so that it is probable that its presence in uranium and thorium minerals is accidental, not genetic. A review of the whole of the cases where two isotopes of the same atomic weight are supposed to occur by branching of the series leads to the conclusion that there is no certain instance of this known, and that both the end-products of thorium are stable forms of lead of the same atomic weight, and therefore indistinguishable from one another. F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes? F. H. LORING (*Chem. News*, 1919, **119**, 62—64. Compare this vol., ii, 313).—When the

isotopic percentages previously given (*loc. cit.*) are plotted against the resistivities of a number of metals, a straight line curve is obtained, which implies that there is a foundation for the theory of whole-number isotopes as applied to ordinary elements. Cadmium constitutes the only exception to this rule, but this may be attributed to the unconfirmed peculiarity in the temperature–resistance curve of this element. The theory of conduction is of interest in connexion with the above-mentioned relationship. Thus, if a small-mass nucleus is so close to a large-mass nucleus that the electronic orbits combine to form a figure of eight, the electrons tending to leave the former to pass round the latter, owing to the greater attraction of the larger mass, then overloading the circuit electrically at any point might give rise to a progressive flow of electrons from atom to atom. On cooling the metal, a point might be reached when further cooling would not improve the contiguity of the orbits, so that perfect conductivity of electricity without any oscillation or vibration of the atoms might take place at a temperature just above absolute zero.

J. F. S.

Behaviour of Non-aqueous Solutions of Salts. A. Thiel (*Zeitsch. Elektrochem.*, 1919, **25**, 214).—Polemical against Beutner (this vol., ii, 263), in which the author maintains that the reasons advanced to explain the electrical conductivity of salts in non-aqueous solvents do not clear up the difficulty, and are not justified on the data put forward. J. F. S.

Activities of the Ions of Strong Electrolytes. Duncan A. MacInnes (*J. Amer. Chem. Soc.*, 1919, **41**, 1086—1092).—A theoretical paper in which it is shown that, since the product of the transport number of the chloride ion and the equivalent conductivity is a constant at a given concentration and temperature for the chlorides of the alkali metals and hydrogen, it may be assumed that the activity of the chloride ion in these solutions is also independent of the nature of the positive univalent ion. On this basis, the activity coefficients of both ions of hydrochloric acid have been calculated for concentrations between 0·001665*N* and 0·100*N*. The potential of the normal hydrogen electrode against the normal calomel electrode has also been calculated, and the value $E=0·2828$ volt obtained. J. F. S.

Generation of Electricity by Atomising Liquids. (Ballo-electricity). IV. C. Christiansen (*Ann. Physik*, 1919, [iv], **59**, 95—100. Compare A., 1916, ii, 75).—A continuation of previously published work undertaken with the object of ascertaining whether isomerides produce the same electric effect when projected against an electrode in a finely atomised stream. The experiments show that *d*-tartaric acid, *l*-tartaric acid, *i*-tartaric acid, and racemic acid in *N*/10-solution produce exactly the same effect, which is very small and approximates in value to that of the inorganic acids. When the above-mentioned acids are mixed with

alcohol or 2*N*-sodium chloride, the effect is much greater in each case; in the case of the alcohol mixtures, the value is the same for each acid, but with the sodium chloride mixtures the values vary slightly. Propionic acid produces a much greater effect than either of the monochloro-substitution products. Propionic acid and α-chloropropionic acid produce a positive effect, whilst β-chloropropionic acid produces a negative effect. The β-compound does not change its effect on keeping, but the α-compound has a decreased effect on keeping. β-Hydroxybutyric acid in *N*/2-solution has a much larger effect than α-hydroxybutyric acid. Substitution of bromine has a different effect than substitution of chlorine on the ballo-electric effect of organic substances. This fact is shown by experiments with bromal hydrate, chloral hydrate, monochloroacetic acid, and monobromoacetic acid. J. F. S.

Generation of Electricity by Atomising Liquids (Ballo-electricity). V. C. Christiansen (*Ann. Physik*, 1919, [iv], **59**, 280—292. Compare preceding abstract).—An instrument (ballometer) is described whereby the charge on particles of a liquid atomised in air, the charge on the air, and the amount of electricity which has escaped from the particles which have been in contact may be measured. J. F. S.

The Electrolytic Potential of Copper in the Presence of Various Electrolytes. P. Benvenuti (*Atti R. Ist. Veneto Sci.*, 1916, **75**, 1317—1329).—This work was started with the idea of producing an electrolytic deposit of an alloy of copper and manganese, but this was afterwards given up as impossible, and the measurements of the potential of copper in the presence of various electrolytes were systematically continued on account of the information thus obtained in regard to the greater or less stability of the complexes produced in this way, and because the data obtained could be utilised in further investigations. The method consisted in connecting the copper electrode, and the electrolyte in which it was immersed, with a normal calomel electrode, and in measuring the *E.M.F.* of the resulting cell by Poggendorff's compensation method. Measurements were made at 15°. The salt of copper was the sulphate. The copper electrode was immersed in this solution with varying quantities of other electrolytes. The results show that, by the addition of these other substances, the potential of the copper increases in the electropositive direction in proportion to the formation of complex ions. In proportion to the increased stability of the complex ions formed, the electrolytes studied arranged themselves in the following order: sodium formate, sodium acetate, ammonium tartrate, hydrochloric acid, potassium bromide, sodium thiosulphate, and potassium cyanide. The author believes that a more extensive study of these phenomena will reveal interesting relations between the nature of electrolytes co-existing in one solution and the stability of the complexes which are formed. Chemical Abstracts

Phenomenon of Electrical Supertension. II. A. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1106—1111. Compare this vol., ii, 8, 91).—A theoretical paper in which the conditions of the supertension of hydrogen generated when metals act on water are considered on the basis of the phase rule.

J. F. S.

Electrolytic Reduction of Arsenic and Arsenious Acids to Arsenic Trihydride at Cathodes of Different Metals. Ludwig Ramberg (*Lunds. Univ. Arsskr.*, N.F., Abt. 2, 1918, **14**, No. 21, 1—47; from *Chem. Zentr.*, 1919, i, 905—906). —A historical résumé of the literature is given, and the newer, quantitative methods are critically discussed. The latter are all unsatisfactory. The discrepancies between the data of various authors are due partly to deficient technique and partly to the unexpectedly great influence of the nature of the surface of the cathode. Certain new types of electrolytic apparatus are described which are chiefly notable for the type and location of the diaphragm. The errors due to the diffusion of compounds of arsenic and to the wandering of the arsenate ion to the anode, together with their dependence on the nature of the material of the diaphragm, have been investigated. It is found that the wandering of the ions is a considerably more important factor than is diffusion, and is so important that the quantitative reduction of arsenic acid to arsenic trihydride can only be effected at cathodes at which the process occurs very rapidly. Arsenic trihydride is estimated by absorption in standard iodine solution and estimation of excess of the latter with standard arsenious acid.

Cathodes of the following metals have been used: mercury, zinc, copper, silver, lead, iron, tin, cadmium, nickel, and platinum. The results are given in a series of tables, from which it appears that the nature of the cathodic surface has a great influence on the reduction of arsenic acid to arsenic trihydride. The process generally takes place far more rapidly at spongy than at polished surfaces. The nature of the surface appears to be less important in the case of arsenious acid, and in any case the polished surfaces are not less effective than the spongy ones.

Different series are obtained for arsenic and arsenious acids when the metals are arranged in order of reducing power, but without regard to their superficial condition. In no case does the order exactly coincide with that derived from consideration of over-voltage, although a certain parallelism exists between the latter and the power of reducing arsenious acid.

Rapid and complete reduction of arsenic acid to arsenic trihydride only occurs at mercury cathodes, although certain amalgamated metals give moderately useful results. On the other hand, a mercury cathode is unsuitable for the reduction of considerable amounts of arsenious acid, since the arsenic is not hydrogenated as rapidly as it is formed; a solid phase of arsenic

arsenic amalgam is thus formed which is only very slowly transformed into arsenic trihydride.

The practical value of the methods is demonstrated by a series of analyses. Estimation of arsenic acid, in amounts containing as much as 50 mg. of arsenic, can be readily effected at mercury cathodes with an error of ±0·1%. Cathodes of lead, silver, or tin are most useful in the estimation of arsenious acid. The supposed superiority of lead for this purpose is not confirmed, and polished tin appears to be the best material. The same accuracy as in the estimation of arsenic acid at mercury cathodes cannot, however, be attained; with increasing quantities of arsenic, the losses become greater, and reach as much as 0·25% with 20 mg. of arsenic. H. W.

Removal of Residual Gases, especially from the Electric Glow Lamp. L. Hamburger (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1062—1077).—By determination of the changes in gas pressure and by spectroscopic observations, it is shown that with the aid of electric discharges phosphorus vapour can be made to react rapidly with all gases except the inert gases. The action observed in the glow-lamp with phosphorus can also be observed with silicates. At high temperatures, silicates undergo fractional distillation. When tungsten and silicates are in contact at a high temperature, a reaction takes place between them by which an alkali metal is liberated. By means of this, as in the case of phosphorus, the residual gases can be removed from glow-lamps with the aid of electric discharges. The reaction between tungsten and glass makes possible the use of this metal for "leading-in" wires. When rapidly cooled, the vaporised silicate has properties different from those of the normal glass, since it is in a supercooled condition, and this condensate can decrease the blackening of the wall of the lamp produced by the vaporised tungsten. If, instead of coating the filament with a silicate, an aluminate, calcium phosphate, magnesium oxide, or silica is substituted, a similar reaction occurs. In the case of silica, it is to be assumed that a trace of free silicon is formed; only quantities of the order 0·001 mg. of silicon show a detectable activity. J. F. S.

Specific Heat of Argon and Several Polyatomic Gases. Wilhelm Heuse (*Ann. Physik*, 1919, [iv], **59**, 86—94).—Making use of the method previously employed (A., 1912, ii, 19; 1913, ii, 183), the author has determined the specific heat of argon, carbon dioxide, nitrous oxide, nitric oxide, methane, acetylene, ethylene, and ethane at temperatures varying from the ordinary temperature to within a few degrees of the condensation point. The following values, among others, have been obtained: argon, c_p 15°, 0·531; −182°, 0·556; carbon dioxide, c_p 20°, 0·846; −75°, 0·768; nitrous oxide, c_p 20°, 0·879; −30°, 0·835; −70°, 0·797; nitric oxide, c_p 15°, 1·012; −45°, 1·001; −55°, 1·014; −80°, 1·024; methane, c_p 15°, 2·22; 5°, 2·20; −30°, 2·13; −55°.

2·11; −80°, 2·11; acetylene, c_p 18°, 1·680; −71°, 1·470; ethylene, c_p 18°, 1·527; −36°, 1·371; −68°, 1·314; −91°, 1·291; ethane, c_p 15°, 1·728; −35°, 1·539; −82°, 1·455. In a large table, the values of the density, specific and molecular heats at constant pressure and constant volume, and the ratio of the specific heats at various temperatures and at zero, are tabulated. J. F. S.

Some Molecular Heats at Very High Temperatures. H. von Wartenberg and G. Witzel (*Zeitsch. Elektrochem.*, 1919, **25**, 209—212).—The molecular heats of the oxides of magnesium, calcium, and aluminium have been determined by burning a mixture of the metal and its oxide in oxygen in a calorimetric bomb. The temperature at which the measurements are made is that of the melting point of the oxide, and this is obtained by using such a mixture of oxide and metal that the oxide is just not melted. Instead of using the oxide as indicator, a mixture of the metal under investigation and finely divided platinum or iridium may be used in such quantities that the metal is just melted. The results obtained represent the upper limit, and are probably accurate to 10—20%; regarded in this way, they are in agreement with the value extrapolated from the curve of values up to 1600°. The following values have been obtained: magnesium oxide, 11·6 cal. at 2780°; calcium oxide, 14·8 cal. at 2552°; and aluminium oxide, 29·1 cal. at 2030°. J. F. S.

The Molecular Heat of Binary Metallic Alloys. Augusto Levi (*Atti R. Ist. Veneto Sci.*, 1916, **75**, 627—632).—The principle of Dolezalek-Schulze for calculating the molecular refraction of binary liquid mixtures is applied to the calculation of the molecular heat of bismuth–tin alloys. p_a and p_b are the masses of the constituents in a gram of the mixture, m_a and m_b the molecular weights, and q_a and q_b the molecular fractions of the constituents.

$$q_a=(p_a/m_a)/[(p_a/m_a)+(1-p_a)/m_b],$$

$$q_b=[(1-p_a)/m_b]/[(p_a/m_a)+(1-p_a)/m_b].$$

If $C_{a,b}$ is the specific heat of the mixture, (1) $C_{a,b}=C_ap_a+C_bp_b$, and for the molecular heat of the mixture, (2) $C_{a,b}(m_ap_a+m_bp_b)=C_am_aq_a+C_bm_bq_b$, in which the first member expresses the molecular heat of the mixture as found by experiment, and the second member the value as calculated by the rule of mixtures. Experiments were carried out by the method of mixtures with alloys of lead and of tin with bismuth. Data indicate clearly the formation of a compound of lead and bismuth when the molecular fraction of lead is 0·44. The eutectic is identical with or close to that mixture which gives maximal molecular heat and produces a compound in the alloy. The curve for mixtures of tin and bismuth is more difficult to interpret and suggests further investigation. Chemical Abstracts.

Latent Heat and Surface Energy. I. D. L. Hammick (*Phil. Mag.*, 1919, [vi], **38**, 240—245).—The author has deduced an

expression connecting the molecular surface energy with the latent heat. This has the form $\rho V/d = L_1 J/6$, in which ρ is the surface energy in ergs per sq. cm., V is the molecular volume, d the molecular diameter, L_1 the internal latent heat per gram-mol. in cals., and J the mechanical equivalent of heat. This equation has been evaluated for a number of gases (6) and organic liquids (23), and is shown to fit the facts remarkably well. A table of the mean diameter of the molecules of the substances concerned is given containing the value deduced from the diffusion, thermal conductivity, refractive index, and the Avogadro constant b.

J. F. S.

Temperature of Explosion for Endothermic Substances. Rasik Lal Datta and Nihar Ranjan Chatterjee (T., 1919, **115**, 1006—1010).

Calculation of the Relation between the Vapour Pressure of a Solid and that of a Supercooled Liquid at Various Temperatures. A. Boutaric (*Compt. rend.*, 1919, **169**, 432—435).—The formula given is $\log_e p_1/p_2 = U_e/2RT \times 1 - T^2/\theta^2$, where p_1 and p_2 are the vapour pressures of the supercooled liquid and solid respectively at $T°$ (absolute), θ the temperature of transformation, and U_e the diminution of total energy at this temperature. In the case of water and benzene, the observed and calculated values agree with one another, but there is a considerable difference between the values for formic acid. W. P. S.

Dependence of the Vapour Tension of Benzene-Toluene Mixtures on the Temperature. Alfred Schulze (*Ann. Physik*, 1919, [iv], **59**, 73—85).—Making use of the vapour pressure measurements of Mangolt (*Sitzungsber. K. Akad. Wiss. Wien*, 1893, **102**, 1071) for mixtures of benzene and toluene, the author has plotted the vapour pressure as a function of the molecular concentration for the temperatures 20°, 30°, 40°, 50°, and 60°. The partial pressures of both constituents are also calculated and plotted. A consideration of the curves, based on the law of mass action, allows conclusions on the molecular complexity of toluene to be drawn. It is shown that at 20° liquid toluene consists of double molecules to the extent of 50%, at 50° to the extent of 8%, and at 60° it is unimolecular. J. F. S.

Vapour Pressure and Affinity of Isotopes. F. A. Lindemann (*Phil. Mag.*, 1919, [vi], **38**, 173—181. Compare this vol., ii, 209).—Though isotopes in principle must be separable both by fractionation and by chemical means, the amount of separation to be expected depends on the way the chemical constant is calculated, and experiments on the vapour pressure and affinity of isotopes would give valuable information on this point. F. S.

The Possibility of Separating Isotopes. S. Chapman (*Phil. Mag.*, 1919, [vi], **38**, 182—186).—A method of separating a mixture of gaseous isotopes, depending on thermal diffusion, is sug-

gested, and from the mathematical examination of the problem it is concluded that it should prove practicable. If the mixture is kept in two communicating vessels maintained at different temperatures, in the equilibrium condition there is a slight excess of the heavier gas in the colder vessel. For the case of a mixture of equal volumes of neon of molecular weight 20 and of the hypothetical meta-neon of molecular weight 22, supposing the mixture to be contained in two bulbs at absolute temperatures 80° and 800°, the cold bulb would contain in equilibrium 48·9% of the meta-neon and 51·1% of neon. This difference of 2·2% is reduced to 1·2% when the proportions of the mixture are as 10:1, and assumes the molecules to behave as elastic spheres. The time taken for the equilibrium to be reached ought not to be unduly protracted, and the operation can be repeated as often as desired on the fractions obtained. F. S.

Free Energy of Dilution of Aqueous Sodium Chloride Solutions. Arthur John Allmand and Wilfrid Gustav Polack (T., 1919, **115**, 1020—1039).

Connexion between the Atomic Weights, Densities, and Heats of Reaction of the Elements. II. Karl Fehrle (*Physikal. Zeitsch.*, 1919, **20**, 330—342. Compare A., 1918, ii, 296).—The formula put forward previously (*loc. cit.*) for calculating the heat of formation of compounds from the molecular weight and the density has been used to calculate the heat of formation of the chlorides, bromides, iodides, oxides, and carbonates of a number of elements of groups I—V. The results indicate that the formula gives values which are in moderate agreement with the experimental values. J. F. S.

Vapour Pressures and Densities of Mixtures of Acetone and Methyl Ethyl Ketone. Tudor Williams Price (T., 1919, **115**, 1116—1126).

Density and Temperature. II. W. Herz (*Zeitsch. Elektrochem.*, 1919, **25**, 215—216. Compare this vol., ii, 268).—The author has calculated the density at the absolute zero (d_0) from the values at the critical temperature ($d_{crit.}$), boiling point (d_b), freezing point (d_m), and at 20° respectively for a number of alcohols (8), esters (13), acids (9), hydrocarbons (13), and halogen-substituted hydrocarbons (4) by means of the formulæ $d_0=3{\cdot}75d_{crit.}$, $d_0=1{\cdot}41d_b$, $d_0=1{\cdot}21d_m$, and

$$d_0=d_t(0{\cdot}77+0{\cdot}64T/T_{crit.}).$$

The values obtained by the various methods are in fair agreement with one another. The density at absolute zero decreases with increasing molecular weight in the series of alcohols, acids, esters, and aromatic hydrocarbons, but rises with increase of molecular weight in the series of paraffins and halogenated benzenes.

J. F. S.

Are the Divergencies of the Atomic Weights from Whole Numbers to be Explained by Isotopy? O. STERN and M. VOLMER (*Ann. Physik*, 1919, [iv], **59**, 225—238).—Experiments are described in which hydrogen and oxygen respectively are generated and the gas allowed to diffuse under atmospheric pressure. The density of the gas is determined before and after a portion has diffused. In this way, it is shown that the whole of the gas has the same density, that is, hydrogen and oxygen are not mixtures of isotopes. It is also shown that every theory of the structure of atoms, based on the Prout hypothesis, must be capable of explaining the divergence of the atomic weights from whole numbers by means of energy differences. J. F. S.

Solubility. III. Relative Values of Internal Pressures and their Practical Application. JOEL H. HILDEBRAND (*J. Amer. Chem. Soc.*, 1919, **21**, 1067—1080. Compare A., 1916, ii, 518; 1918, ii, 36).—Various independent methods are discussed for calculating the internal pressures of liquids, and although the values obtained differ considerably, yet they are found to be closely parallel. Tables of the relative values are given in the paper for non-polar substances. Other substances may be tabulated with reference to these substances by knowing their densities, together with either surface tension, boiling point, the constant a of the van der Waals' equation, the coefficient of expansion, or the last together with the compressibility. The use of these values is discussed in connexion with predictions concerning the solubilities of solids, liquids, and gases, the distillation of liquid mixtures, molecular weights and association, deviations from the law of mass action, partition coefficients, and the choice of solvent in recrystallisation. J. F. S.

Adsorption Isotherm at Low Concentrations. A. M. WILLIAMS (*Proc. Roy. Soc. Edin.*, 1919, **39**, 48—55).—A theoretical paper in which it is shown that for very small adsorptions the adsorption law has the form $\alpha=\alpha_0 c$ for both gases and solutions. From this expression, adsorption curves have been produced for solutions and found to agree with the curves obtained by Trouton for acetic acid and charcoal (Rep. Brit. Assoc., 1911, 328) and Schmidt-Walter for water, benzene, and toluene (A., 1914, ii, 542). J. F. S.

Surface Tension and Chemical Interaction. G. N. ANTONOFF (*Phil. Mag.*, 1919, [vi], **38**, 417—419. Compare A., 1918, ii, 437).—A theoretical paper in which it is shown that the results obtained in the previous paper (*loc. cit.*) can be obtained whatever law of molecular action is used as the basis of calculation. The results previously obtained depend on the assumption that molecular action takes place according to an inverse fourth-power law. It is now shown that if an inverse nth power law be assumed, the expressions for surface tension (α) and internal

pressure (P), respectively, would be $\alpha = kp^{(n+1)/3}$ and $P = 2kp^{(n+2)/3}$. Thus the formula connecting both quantities is $P = k\alpha p^{1/3}$, where $k = 2$, as in the previous paper. The relationship $\alpha_{12} = \alpha_1 - \alpha_2$ does not depend on the law of molecular attraction, but is a result of a certain chemical interaction between the liquids forming the solutions which enables the heterogeneous system to become stable and prevents both layers from mixing.

J. F. S.

Diffusion of Double Salts. D. Merrill Torrance (*Chem. News*, 1919, **119**, 66—67).—From experiments on the rate of diffusion of potassium antimonyl tartrate and potassium sodium tartrate, it is shown that the antimony does not diffuse through with three times the velocity of the potassium, as was expected. The experiments also show that the rate of diffusion through dead or artificial tissue is very different from that through living tissue.

J. F. S.

Velocity of Diffusion. Hans Bauer (*Physikal. Zeitsch.*, 1919, **20**, 339—340).—Polemical. A number of remarks to the work of Franks (this vol., ii, 100) on the same subject. J. F. S.

Reactivity of Powdered Glasses. Paul Nicolardot (*Compt. rend.*, 1919, **169**, 335—337).—Account must be taken of the degree of fineness of the powder in testing the resistance of glass to solvent action by boiling the powdered material with water and with dilute hydrochloric acid, otherwise concordant results will not be obtained. Powders of various sorts of glass were prepared in three degrees of fineness by sifting, the ratios of the surfaces being substantially 1 : 2·84 : 12·8, and the loss in weight of each after boiling in a platinum vessel for three hours with pure water and with N/10-hydrochloric acid was determined. From the tables given, the following examples may be quoted, the figures being the loss per 1000 of the whole glass and the three powders mentioned above:

Jena glass to water,	0·09, 0·25, 0·75,	2·75.
„ „	N/10-HCl, 0·03, 2·00, 5·25,	40·25.
Thuringian (R) glass to water,	0·03, 0·25, 0·75,	5·25.
„ „ „	N/10-HCl, 0·01, 0·75, 3·75,	12·50.
A French glass to water,	0·11, 1·00, 2·00,	10·00.
„ „	N/10-HCl, 0·02, 0·25, 1·75,	17·00.

It will be seen that, contrary to observations on the whole glass, the powder in nearly all cases is attacked more by hydrochloric acid than by water. Further, whilst water attacks powders of different fineness to practically the same extent per unit of exposed surface, the diluted hydrochloric acid in general attacks the finest powder more vigorously than the others in proportion to its surface area. G. F. M.

Influence of Neutral Chlorides on Chromium Chloride Solutions. M. E. Baldwin (*J. Amer. Leather Chem. Assoc.*, 1919, **14**, 10—19; from *Chem. Zentr.*, 1919, i, 805—806).—It has

been previously shown (Thomas and Baldwin, *J. Amer. Leather Chem. Assoc.*, 1918, **13**, 192, 248) that the acidity of solutions of chromium sulphate, determined by the electrometric process, is increased by addition of chlorides and is primarily diminished, but subsequently raised by addition of sulphates. The influence of the chlorides of sodium, potassium, ammonium, lithium, and barium on the acidity of solutions of chromium chloride has now been investigated, the experiments being conducted immediately after preparation of the solutions and also after preservation during fifty days. The results show that the hydrogen-ion concentration of chromium chloride solutions is increased by the presence of neutral chlorides, although the total amount of acid hydrogen remains constant. When the salts are arranged in order of increasing effect, the following series is obtained: (KCl,NH_4Cl), $NaCl$, $LiCl$, $BaCl_2$. To determine whether the hydrolysis of chromium chloride plays a part in these results, a similar series of experiments has been conducted with hydrochloric acid solutions of approximately the same hydrogen-ion concentration, when similar effects are observed. It is noticeable that the different salts increase the hydrogen-ion concentration in proportion to their capacity of uniting with a larger number of molecules of water in accordance with the theory of hydrates. Comparison of the results obtained with solutions of chromium chloride and hydrochloric acid show that the phenomenon does not depend on the hydrolysis of the former, since the changes in either case are of the same order and approximately of the same magnitude. On the other hand, the changes which occur after some time in the "actual acidity" of chromium chloride solutions appear to depend on the nature and amount of chromium chloride present. An explanation of the increase in the hydrogen-ion concentration of chromium chloride solutions caused by the addition of neutral chlorides has been advanced by Wilson and Kern (*J. Amer. Leather Chem. Assoc.*, 1917, **12**, 455), who suppose that the amount of water available as solvent is diminished by the combination of the salts and their ions with a portion of the water. H. W.

Isomeric Alloys. G. Tammann (*Nachr. Ges. Wiss. Göttingen*, 1918, 332—350; from *Chem. Zentr.*, 1919, iii, 89—90). —Normal distribution of atoms cannot occur when two metals separate simultaneously at a temperature at which diffusion is impossible in the mixed crystal; in these circumstances, the arrangement is probably irregular. The crystalline or cryptocrystalline products obtained when two metals separate from a solution have been investigated to some extent, but exact comparison with the series of alloys obtained from the molten metals has not previously been possible, since the properties of the latter were only incompletely known. Binary, crystalline, metallic mixtures can be obtained from galvanic cells formed by placing the two metals in a solution of the less noble, by the electrolysis of a solution of the two metals, by precipitation of the one metal on the

other, and by reduction of the solution of the two metals. Before comparing the properties of these mixtures with those obtained from molten masses, it is desirable to obtain an idea of the capacity for diffusion of a metal deposited on a cathode of a second metal; this power is a characteristic of the nascent atom, and is to be distinguished from the mobility of two kinds of atom in a mixed crystal. If a cell consisting of the two metals immersed in a solution of the less noble metal is short-circuited, cations of the latter are deposited on the more noble metal. If, now, diffusion proceeds at a negligible rate, the original potential of the cell is rapidly regained when the circuit is opened; when diffusion is more rapid, the recovery is gradual. If the potentials are measured by the electrometer, the method gives a very sensitive means of detecting diffusion of the less noble into the nobler metal. Solutions of cadmium and copper sulphates have been electrolysed with the object of obtaining information of the effect of the composition of a mixed electrolyte and of the current density on the composition of the cathodic deposit. By suitable variation of these factors, deposits can be obtained the tensions of which vary between zero and the tension of copper towards cadmium. The Cu–Cd alloys obtained from the molten metals behave quite differently, and therefore cannot be identical with the mixtures prepared electrolytically. The relative affinity of the two metals governs the content of precipitating metal in the precipitated metal. When the two metals can unite with one another, the deposit of the nobler metal from the solution is rich in less noble metal; when, however, a compound is not formed, the noble metal is deposited either free from or admixed with but small amounts of the less noble metal. In certain cases, the composition of the precipitate corresponds with that of one of the compounds obtained from the molten mixtures (for example, Cu_2Cd_3, $CuCd_3$, Cu_3Sn); with other pairs of metals, the composition of the precipitates varies greatly in different preparations (with Cu–Zn, Ag–Zn, Ag–Cd). Even in those cases (Cu–Au, Fe–Pt) in which the two metals form a continuous series of mixed crystals from their molten mixtures, the precipitate is rich in the less noble metal. The precipitates from less noble metals appear to be identical with those obtained by the electrolysis of mixed electrolytes; in each case, the composition depends on that of the electrolytes and on the current density at the place of precipitation. The alloys obtained from molten metals are not identical with those prepared by precipitation from mixed electrolytes; this is shown in detail in the cases of Cu_3–Sn, Au–Ag, Zn–Cu. H. W.

Alteration in the Chemical Behaviour of Metals and their Mixed Crystals by Mechanical Working. G. Tammann (*Nachr. Ges. Wiss. Göttingen*, 1918, 351—361; from *Chem. Zentr.*, 1919, iii, 90—91).—The energy content of a piece of metal is increased by cold working; the methods of estimating this increase are described. Permanent deformation of a piece of metal

causes an increase in its energy which depends on the extent of deformation, the degree of working, and also on the nature and temperature of the metal. The mechanical process leads to a disintegration of the metal which corresponds with an increase in potential energy, whilst the latter is also augmented by processes which can occur within the atom itself. A cold-worked metal is less noble in the hard than in the soft condition. Since those layers which lie on the surface are alone affected, a piece of metal which is superficially hardened, but internally still soft, can behave as less noble than a thoroughly hardened piece. These conclusions have been verified by observations on silver wires which had been worked in different manners. The supposedly exceptional position of bismuth could not be confirmed. The increase in the rate of solution of iron caused by cold-working is probably due to the formation of twin lamellæ in the iron crystals. The action limits of chemical reagents on alloys of gold with copper and silver are altered by mechanical working of the alloys. Rolling and hammering imparts increased chemical activity to Ag–Au alloys, which is noticeable when the gold content is far greater than that which corresponds with the reaction limit in soft alloys. Polishing of the alloys has an effect similar to that of converting them into thin foil. The unexpectedly great displacement of the action limits by mechanical working can only be explained by the assumption of an alteration in the properties of the gold atoms; the latter, in consequence of displacement, are much less firmly retained than formerly, and consequently separate more readily from the lattice after removal of the active atoms. An agent, the action of which surpasses the natural limit, is able to remove the protecting gold atoms from the lattice when their number corresponds with that of the normal reaction limit. H. W.

Atomic Structures of Non-metallic Mixed Crystals. G. Tammann [with K. W. Schmidt] (*Nachr. Ges. Wiss. Göttingen*, 1918, 296—318; from *Chem. Zentr.*, 1919, i, 782—784). —In the absence of abnormal double refraction, the occurrence of definite reaction limits enables the distinction to be made between normal and irregular distribution. The phenomenon has been utilised for the purpose of gaining insight into the arrangement of the molecules in non-metallic mixed crystals. The capacity for diffusion of the two components must also be taken into account, since conclusions, based on the absence of reaction limits, are only valid when the diffusion is negligibly small. Reaction limits similar to those observed with metals occur in mixed crystals of salts when they are prepared from the molten materials and tempered for a sufficient period. The action of water on mixed crystals of sodium and silver chlorides has been investigated, both salts being completely miscible in all proportions in the liquid and crystalline conditions. Crystals with 1—0·75 mol. AgCl scarcely yield any sodium chloride to water; those with 0·75—0·625 mol. AgCl give part of the salt, whilst water removes the sodium

chloride completely from those containing 0·625 mol. AgCl and less. The observations thus closely resemble those made on the extraction of Au–Cu and Au–Ag alloys with boiling nitric acid. An explanation of the behaviour of the salts is based on a conception of the distribution of the silver, sodium, and chlorine atoms in the space lattice. This is determined for sodium chloride by means of the Röntgen spectrum, and since sodium chloride and silver chloride form an unbroken series of mixed crystals, a similar lattice may be assigned to the latter. The normal distribution of the different atoms in the assumed structure is indicated for the molar fractions 5/8 and 6/8. Diffusion in mixed crystals shows important quantitative differences from that observed with metals. In the neighbourhood of the melting point, the process occurs much more rapidly in metallic than in non-metallic mixed crystals, and is also more noticeable at temperatures considerably below the melting point. This dictum is not based on quantitative determination of the rate of diffusion, but depends on phenomena (such as the rapidity with which layers of mixed crystals become homogeneous), from which an idea of the rate of diffusion can be obtained. Mixed crystals, the content of which in inactive material is greater than that of the reaction limit at high temperature, deposit a portion of the active material as a result of diffusion, the process occurring more rapidly with increasing temperature. If crystalline powders of two substances, one of which is colourless and the other coloured, are pressed together, an idea of the relative rates of diffusion can be obtained by observation of the change in colour at the originally sharp line of contact. With electrolytes, the conductivity, with similar drop in voltage, is a measure of the mobility of the ions involved in the process. Noticeable electrolytic conductivity is an indication of incipient diffusion. With increasing temperature, the conductivity increases from negligible to very considerable values near the melting point. The great differences in the relative rates of diffusion in metallic and non-metallic mixed crystals are shown by the fact that definite reaction limits are much more rapidly developed by tempering with the former than with the latter. The diffusion of compressed substances has been investigated with the following pairs of compounds: dibenzyl and azobenzene, stilbene and azobenzene, sodium sulphate decahydrate and sodium chromate, potassium perchlorate and potassium permanganate, magnesium sulphate heptahydrate and nickel sulphate heptahydrate, mercuric bromide and mercuric iodide decahydrate. Diffusion of the coloured into the colourless substance is only noticeable with isomorphous crystals, the melting points of which are only slightly higher than the temperature of the experiment; even when this is the case, the process only occurs very slowly. The application of the laws of dilute solution to the solubility and vapour tension isotherms of series of mixed crystals is discussed, but the application of the theory is rendered impossible, since equilibrium between solution and mixed crystal is not attained in any reasonable time when equilibrium is deduced

from the normal arrangement of the crystal lattice. Differences in distribution in the lattice cause mixed crystals of similar composition to form normal and abnormal isomerides, which are differently attacked by solutions. Thus mixed crystals of silver and sodium nitrates were prepared (1) by very slowly cooling a mixture of the molten salts, and (2) by cooling a solution of the two salts in aqueous alcohol. When the two products were treated with a saturated solution of sodium nitrate, considerably greater amounts of silver nitrate were dissolved from the latter than from the former. A second example of isomeric mixed crystals occurs with the chlorides of silver and sodium; they are distinguished by the difference in the rates at which sulphide is formed on them by the action of a solution of sodium chloride containing ammonium sulphide. H. W.

Chemical and Galvanic Properties of Mixed Crystals and their Atomic Structure. G. Tammann (*Zeitsch. anorg. Chem.*, 1919, **107**, 1—239).—A detailed account is given of the author's previously published researches on the discontinuous properties of mixed crystals, and particularly of simple binary alloys, an explanation of these properties in terms of the space-lattice theory being fully discussed. (Compare A., 1917, ii, 448; 1918, ii, 209, 225, 235, 443, 445, 447.) E. H. R.

Method of Growing Large Crystals from Solution. R. W. Moore (*J. Amer. Chem. Soc.*, 1919, **41**, 1060—1066).—The author has produced perfect crystals of potassium sodium tartrate nearly 10 cm. long by the following method. A saturated solution at 35—40° was made up, removed from the excess of solid, heated to 7—8° above the saturation temperature, and rapidly filtered through paper, care being taken that the temperature did not fall to less than 4—5° above the saturation temperature. Small seed crystals are suspended on threads in a jar and the salt solution poured in. The jar is covered with a glass plate and placed in a water-bath 0·5° above the saturation temperature of the solution. The temperature is allowed to fall to the saturation temperature, and then by means of a sensitive thermo-regulator the rate of cooling is regulated to 0·1° per day until the crystals have become perfect. This usually requires one day. Then the temperature is allowed to fall 0·2° per day until the crystals are 1·8—2·5 cm. long, after which the rate of cooling is increased to 0·5—0·6° per day. When the bath has reached the ordinary temperature the crystals are removed and dried by wiping with a soft cloth. J. F. S.

The Effect of Ions of Sodium Chloride and Calcium Chloride on the Electrical Conductivity of Certain Colloidal Mixtures. Newton Baldwin Green (*Plant World*, 1918, **21**, 303—317).—Cylinders of colloidal gel, such as gelatin, or mixtures of gelatin, agar, and whole wheat flour, are readily penetrated by the ions of sodium chloride and calcium chloride; the initial rate of penetration is not the same for both salts, but after

several hours the rates become identical. At the beginning sodium chloride diffuses more rapidly than calcium chloride, the ratio of the two rates being approximately 10:8. Because of the greater adsorption of the cation in the case of calcium chloride the diffusion of ions is hindered to some extent. This occurs at the surface of the colloid, and may help to account for Osterhout's observation of the decrease in permeability when calcium salts are used. When one salt is allowed to penetrate the colloid for a time and then a second salt substituted, the rate of penetration of the ions of the latter seems to be unaffected by the presence of the former. A mixed solution of sodium chloride and calcium chloride gives a curve of fall of resistance similar to that of either of the constituents alone. It approaches in value more nearly the curve of the predominant salt. The ions of sodium chloride and calcium chloride do not antagonise one another as regards their penetration into certain colloidal gels, notably gelatin, and mixtures of gelatin, agar, and whole wheat flour. Determinations of electrical resistance were made of solutions of gelatin to which had been added salts in varying concentrations. The purpose of these determinations was to show whether electrical resistance varies directly with the precipitability of the gelatin as determined by Fenn. The electrical resistance of the gelatin was found to vary directly with the precipitability, which is greatest at the isoelectric point. The isoelectric point occurs when the unadsorbed positive and negative ions of the added salts balance one another. It is assumed that balanced solutions owe their effectiveness to the fact that the protoplasm adsorbs from them equal numbers of positive and negative ions, thus bringing the condition to the isoelectric point, at which there is greatest ionisation of the protein, greatest amount of precipitation, and greatest (or normal) permeability.

CHEMICAL ABSTRACTS.

The Influence of Electrolytes on the Electrification and the Rate of Diffusion of Water through Collodion Membranes. JACQUES LOEB (*J. Gen. Physiol.*, 1919, **1**, 717—745).—The rate of diffusion of water through a collodion membrane separating the pure solvent from a solution depends on two kinds of forces. First, those of gas pressure which are clearly recognisable in the case of solutions of non-conductors, and secondly, electrical forces which become predominant in the case of low concentrations of solutions of electrolytes. In the diffusion of water through a collodion membrane into a solution of an electrolyte the water molecules are either positively or negatively charged according to the nature of the electrolyte in solution, and these charges are a factor in the rate of diffusion.

Solutions of neutral salts possessing a univalent or bivalent cation influence the rate of diffusion of water through a collodion membrane as if the water particles were charged positively, and were attracted by the anion and repelled by the cation of the electrolyte. The same rule applies to solutions of alkali. Solutions of neutral or acid salts possessing a tervalent or quadrivalent cation

influence the rate of diffusion as if the particles of water were charged negatively, and solutions of acids obey the same rule.

It is experimentally shown that the assumption of a difference in sign of the charge of water molecules (according to the two rules just mentioned) explains all the phenomena that can be observed.

A method is given by which the strength of the attractive electric force of electrolytes on the molecules of water can be roughly estimated and the results of these measurements are in agreement with the two rules. The electric attraction of water molecules by electrolytes increases with an increase in the concentration of the electrolyte, but more rapidly at low concentration than at high concentrations. A tentative explanation for this phenomenon is offered. The rate of diffusion of an electrolyte from a solution to pure solvent through a collodion membrane seems to obey largely the kinetic theory. J. C. D.

Colloid Chemistry of Congo Rubin. Theory of Indicators and the Theory of the Colour Change of Organic Substances. Wolfgang Ostwald (*Koll. Chem. Beihefte*, 1919, **10**, 179—288. Compare this vol., ii, 187).—A long theoretical discussion, together with some experimental data, from which it is shown that in the exceptional case of congo rubin variations in the degree of dispersity play the main part in the variations of colour during neutralisation of an acid solution by alkali. It is not to be expected that among the numerous organic colour substances congo rubin alone shows this peculiarity. Consequently, the author still maintains the correctness of his statement (A., 1912, ii, 439) on the basis of the present and previous results. This statement is reiterated in the form: "In the colour change of organic substances, such as indicators, colloid and, in general, dispersoid chemical processes play an important part and in many the controlling part."

J. F. S.

Quinone-phenolate Theory of Indicators. A Spectrophotometric Method for Measuring the Concentrations of the Quinoidal and Lactoidal Salts and the Equilibrium and Affinity Constants of the Phenolphthaleins and Phenolsulphonphthaleins. R. T. Birge and S. F. Acree (*J. Amer. Chem. Soc.*, 1919, **41**, 1031—1050).—Equations are deduced expressing the relationship between the specific absorption index, the specific colour intensity, and the percentage of intensity of coloured quinone–phenolate salt respectively with the equilibrium and affinity constants of the two acid groups of phenolphthalein and phenolsulphonphthalein indicators. A spectrophotometric method is proposed for measuring the concentration of the monobasic, yellow quinone phenol salt and of the dibasic intensely coloured quinone–phenolate salt in any solution, and the percentage of any indicator transformed into the quinone–phenolate salt in alkaline solution. By the use of the equations developed and the experimental data of Howe and Gibson (*Phys. Rev.*, 1918, **10**, 767) and of the authors it is shown that sulphonphthalein indicators are

transformed, practically completely, into quinone–phenolate salts, and are therefore very fine, intensely coloured indicators. Phenolphthalein is changed to the extent of only about 44% into the intensely coloured quinone–phenolate salt, the remainder forming the colourless lactoidal and hydrated salts. Tetrachloro-, tetrabromo-, and tetraiodo-phenolphthalein form only about 1—2% of the intensely coloured quinone–phenolate salt, the remaining 98—99% forming the colourless lactoidal or hydrated salts. These indicators are therefore very poor for analytical work. The introduction of 4 atoms of chlorine into the phthalic acid residue of phenolphthalein makes phenoltetrachlorophthalein an excellent indicator, which changes to the extent of 90% into the intensely coloured quinone–phenolate salt. The introduction of halogens into the phenol groups of phenoltetrachlorophenolphthalein gives bromo- and iodo-derivatives, which can only give 17% and 40% respectively of the highly coloured salt in alkaline solution. The spectrophotometric method used in conjunction with the mass action equations gives an approximate measure of the real equilibrium and affinity constants of the two acid groups of indicators of the phenolphthalein and the phenolsulphonphthalein types. The disappearance of the violet band λ 2300 for phenolsulphonphthalein indicates that in alkaline solution the quinone or quinone–phenol group is changed into a quinone–phenolate complex ion like the intensely coloured double compounds made by Jackson (A., 1896, i, 293) by the union of *p*-benzoquinone and phenolates. J. F. S.

Metastable Unmixing and the Classification of Binary Systems. F. E. C. Scheffer (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1055—1056).—A criticism of Buchner's classification of systems in which, in addition to two liquid phases, compounds also occur, and a consideration of the form assumed by the critical line in three phase systems, when unmixing occurs. J. F. S.

The Ternary System, CaO–MgO–SiO_2. J. B. Ferguson and H. E. Merwin (*Amer. J. Sci.*, 1919, [iv], **48**, 81—123).—Cooling curves have been prepared for the ternary system lime, magnesia and silica; the various products have been examined microscopically. The following substances occur as crystalline primary phases: lime; magnesia; silica (tridymite and cristobalite); pseudowollastonite, α-CaO,SiO_2; $3CaO,2SiO_2$; α- and β-$2CaO,SiO_2$; MgO,SiO_2 (clino-enstatite); forsterite, $2MgO,SiO_2$; diopside, $CaO,MgO,2SiO_2$; $5CaO,2MgO,6SiO_2$, and $2CaO,MgO,2SiO_2$. The melting point of $2CaO,MgO,2SiO_2$ is 1458°±5°, and the decomposition temperature of $5CaO,2MgO,6SiO_2$ is 1365°±5°. In addition to these, crystals representing five solid solutions appear as primary phases. These are, (i) a complete series with clino-enstatite and diopside as end members, generally known as pyroxenes; (ii) the pseudowollastonite solid solutions the compositions of which form an area bounded by the following lines: (*a*) the CaO,SiO_2–$CaO,MgO,2SiO_2$ line; (*b*) a line running from the composition

CaO, 44·4; MgO, 3·1; SiO_2, 52·5, on the above-mentioned line across to the composition CaO, 46·7; MgO, 3·5; SiO_2, 49·8 on the CaO,SiO_2–$2CaO,MgO,2SiO_2$ line; (*c*) then either the last-mentioned line back to CaO,SiO_2, or, more probably, an approximate continuation of line *b* to about the composition CaO, 50; SiO_2, 50, on the side line. (iii) The wollastonite solid solutions; these extend to about 17% diopside or 3·2% magnesia at the higher temperatures. The most concentrated of these solid solutions along the diopside line (the 17% line) decomposes at 1340°±5°, and this solid solution is the only one represented on the liquidus. (iv) The

$$5CaO,2MgO,6SiO_2$$

solid solutions. Only a few of these solid solutions which are decomposed at the temperatures near the decomposition temperature of the pure compound, are stable in contact with a suitable liquid. (v) Certain members of the monticellite solid solutions. Monticellite takes up forsterite in solid solution to the extent of about 10%, and the decomposition temperature of the solution is thereby raised. Monticellite itself probably decomposes at too low a temperature ever to occur as a primary phase. The temperature–concentration relations of the liquids which may be in equilibrium with each of these phases have been thoroughly investigated by means of the quenching method, and the results obtained have been correlated with the existing data on the remainder of the ternary system. The compounds $5CaO,2MgO,6SiO_2$ and $2CaO,MgO,2SiO_2$ have not been prepared previously. Attempts to prepare a compound of the formula $8CaO,4MgO,9SiO_2$ (Schaller's åkermanite) gave negative results. The monticellite solid solutions and the compound åkermanite are discussed at length. Experiments were made on the tridymite–cristobalite inversion temperature, which was found, for this system, to be below 1500°; this is approximately in agreement with Fenner's original value of 1470°. The great sluggishness of the inversion precluded a more exact determination. J. F. S.

Critical Solution Temperature of a Ternary Mixture as a Criterion of Purity of Toluene. Kennedy Joseph Previté Orton and David Charles Jones (T., 1919, **115**, 1055—1070).

Hydrolysis of some Metallic Acetates. N. Löfman (*Zeitsch. anorg. Chem.*, 1919, **107**, 241—264).—For the determination of the degree of hydrolysis of a large number of metallic acetates use has been made of the method of Westerberg (*Arkiv. Kem. Min. Geol.*, 1917, **6**). The method consists in shaking a quantity of ether with successive portions of the acetate solution until equilibrium is reached and estimating the acetic acid content of the ether. The distribution-coefficient of acetic acid between water and ether being known, the degree of hydrolysis of the salt can be calculated. Fresh determinations of this coefficient have been made. For dilutions less than $1/15N$ in the aqueous layer it has been found that the distribution-coefficient is independent of the concentration, and for temperatures from 10° to 25° can be expressed by the formula $k=1·89+0·011t$. Double molecules of acetic acid are present in the

ether layer. The presence of acetates increases slightly the value of the coefficient, but not enough to affect appreciably the accuracy of hydrolysis determinations of the acetates.

The degree of hydrolysis of the following acetates has been determined: ammonium, sodium, magnesium, aluminium, chromium, manganese, ferrous, ferric, cobalt, nickel, copper, zinc, silver, cadmium, lanthanum, mercury, and lead. In the case of ammonium acetate the hydrolysis was also determined from measurements of the distribution of ammonia between water and air, and by determining the hydrogen-ion concentration of the acetate solution, the results showing very good agreement among themselves and with the theoretical value. The degree of hydrolysis is independent of the concentration except with ferric and aluminium acetates, the abnormal behaviour of which is attributed to the formation of colloidal hydroxides. E. H. R.

Quantitative Measurements of the Fission of Hexamethylenetetramine. Paul Trendelenburg (*Biochem. Zeitsch.*, 1919, **95**, 146—163).—The rate of fission of hexamethylenetetramine into formaldehyde and ammonia is greatly increased at high concentrations of hydrogen ion. Thus, it is completely hydrolysed by treatment with 0·1*N*-hydrochloric acid for six hours at 38°. With decreasing hydrogen-ion concentration the rate of decomposition falls, but not proportionally, being slightly slower. In neutral solutions about 1% of the hexamethylenetetramine is hydrolysed on being kept at 38° for six hours. A negative result is only obtained when the solution is distinctly alkaline. From these results it follows that this substance is decomposed to no inconsiderable extent in the stomach. Even slight decomposition probably occurs in the mild alkalinity of the intestinal contents or body fluids. The value of the base as a means of disinfecting the bladder contents depends on the reaction of the urine. J. C. D.

Active Substance in the Iodination of Phenols. Victor Cofman (T., 1919, **115**, 1040—1049).

Influence of Hydrogen Sulphide on the Occlusion of Hydrogen by Palladium. Edward Bradford Maxted (T., 1919, **115**, 1050—1055).

Catalytic Actions at Solid Surfaces. I. Hydrogenation of Unsaturated Fats in the Liquid State in Presence of Nickel. E. F. Armstrong and T. P. Hilditch (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 137—146).—Experiments on the rate of hydrogenation of a number of unsaturated fatty oils in presence of finely disseminated nickel have revealed a close analogy between this reaction and the hydrolysis of glucosides in presence of enzymes. The experiments were made with olive oil, cotton-seed oil, whale oil, and linseed oil at about 180°, the rate of hydrogenation being determined by measuring the volume of hydrogen entering and leaving the system by means of water meters. The time–absorption curves,

except in the case of olive oil, are all characterised by an initial linear segment, followed by an abrupt change of direction to a segment of gentler slope, also linear at first but subsequently more or less curved. The position of the point of inflexion of these curves gives the clue to their interpretation. The inflexion takes place on each curve, approximately, at a point when only 10—20% of the glycerides present is derived from acids less saturated than olein. In the case of olive oil this point is reached very soon after the start, and so is difficult to identify on the curve. The curves never approach the logarithmic type required for a unimolecular reaction. The two linear portions represent (1) the hydrogenation of glycerides less saturated than olein, and (2) the hydrogenation of olein itself. Since they are linear they must represent a change in which the acting mass is constant, and, after a reasoned consideration of the possibilities, it is concluded that it is the action of the catalyst that is represented, and, moreover, that the formation of an unstable complex between the nickel and the unsaturated compound must be involved in the reaction.

It has been shown by H. E. Armstrong and others (A., 1913, i, 781) that the hydrolysis of carbamide by urease, and probably most other enzymic reactions, take place at a linear rate, when allowance has been made for the influence of the products of change. The hydrogenation curves show a general resemblance to those obtained in the case of enzymes, and the mechanism of the reaction is probably similar in the two cases, involving the formation and subsequent decomposition of an unstable compound. In each case the interchanges take place in an electrolytic circuit in which the interacting substances and the catalyst or enzyme are all comprised. The action takes place entirely at the surface of minute particles, and the activity of the catalyst depends entirely on the production of the maximum surface and the avoidance of impurities likely to destroy or dirty this surface. E. H. R.

Catalysis. VI. Temperature-coefficients of Heterogeneous Reactions. NILRATAN DHAR (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1042—1047. Compare T., 1917, **111**, 707).—A theoretical paper in which it is shown that it is impossible to establish a relation between the order of a reaction and its temperature-coefficient in heterogeneous systems. The temperature-coefficients of catalysed and non-catalysed reactions are also considered. J. F. S.

Neutral Salt Catalysis [Corrections]. HERBERT S. HARNED (*J. Amer. Chem. Soc.*, 1919, **41**, 1092).—A correction of a previous paper under the same title (compare A., 1918, ii, 436). The following corrections are made: p. 1463, the equation $H_2O_2+IO'=H_2O+I'+O_2$ instead of $H_2O_2+IO'=H_2O+IO_2'$; p. 1477, E_t-E_l instead of E_l+E_t; p. 1478, in table VII all figures in the column E_l should be positive instead of negative, and the column E_t+E_l should be E_t-E_l; and on p. 1479 in table VIII in the column $K\times10^2/a$, 14·14 should be substituted for 13·14.

J. F. S.

Elements in the Order of their Atomic Weight. RAYMOND SZYMANOWITZ (*Chem. News*, 1919, **119**, 58—59. Compare A., 1918, ii, 436).—A further discussion on the atomic weights of the elements based on the condensation theory of their formation.

J. F. S.

The Position of the Electron Orbits in the Atom and the Periodic System of the Elements. P. EHRENFEST (*Chem. Weekblad*, 1919, **16**, 1037—1044).—A lecture delivered before the Nederlandsche Chemische Vereeniging in Maastricht. W. S. M.

Mathematical Investigation of the Stability of A. W. Stewart's Atom. LEONARD C. JACKSON (*Phil. Mag.*, 1919, [vi], **38**, 256—266).—A mathematical paper in which the stability of the atom as conceived by Stewart (A., 1918, ii, 395) is considered. The conditions for the equilibrium and stability of the atom are obtained, and they are applied to several special cases for the helium, lithium, and glucinum atoms. It is found that, in each case tried, equilibrium cannot be maintained indefinitely for the inner ring of negative electrons, even in the entire absence of external perturbing forces. Thus, on the atomic theory considered, instability is placed to the account of those elements which are found to be the least stable in reality. The second alternative put forward by Stewart has not been investigated mathematically, and in view of the fact that the Stewart atom explains physico-chemical facts so well, the author points out that some such alternative suggestion may be reasonably expected to give an atom which is more amenable to ordinary dynamics and more successful in explaining physical phenomena. J. F. S.

Structure of the Atomic Nucleus and its Tendency to Disintegrate. W. KOSSEL (*Physikal. Zeitsch.*, 1919, **20**, 265 – 269).—A theoretical paper in which the view is advanced that elements of even atomic number up to the value 20 are composed entirely of helium nuclei; beyond this point, the atomic weights indicate the possibility of mixtures. Various cases are considered where α- and β-disintegrations may occur. The author introduces a function z which depends on the atomic weight, and is represented by $z=A/2-N$, where A is the atomic weight and N the atomic number. The value of z is plotted against the atomic weight, and the curve thus obtained shown to be practically horizontal up to atomic weight 40, and then it rises in practically a linear manner.

J. F. S.

Constitution and Structure of an Atom of Nitrogen. HAWKSWORTH COLLINS (*Chem. News*, 1919, **119**, 29—30).—A theoretical paper in which it is suggested that the nitrogen atom is made up of two hydrogen atoms and one carbon atom. This result is reached from a consideration of the theoretical and experimental

results of Rutherford, J. J. Thomson, and Collie and Patterson, and from a consideration of the relative volumes of the atoms. Thus, the relative volume of an atom of carbon at 15° in all carbon compounds in which the element is united to other elements by single bonds is 0·71. The relative volume of an atom of hydrogen at 15° when united to an atom of carbon in the "first position" is always 15·25. The relative volume of an atom of hydrogen at 15° when united to an atom of carbon in the "fourth position" is always 5·76. The relative volume of an atom of nitrogen at 15° when united by single bonds to other elements is 0·71. The relative volume of an atom of nitrogen at 15° when united to a carbon atom by three valencies is $15·96 = 0·71 + 15·25$. The relative volume of an atom of nitrogen at 15° in nitrates and nitrites is $21·72 = 0·71 + 15·25 + 5·76$. The above results show that the two hydrogen constituents of nitrogen are capable of being expanded from negligible volume to 15·25 and 5·76 respectively.

J. F. S.

Characteristic Ultra-red Frequencies of Diatomic Bohr Gas Molecules and the Specific Heat at High Temperatures. Gerda Laski (*Physikal. Zeitsch.*, 1919, **20**, 269—274).—A mathematical paper in which it is shown that, in the sense of Bohr's theory, the molecular model of nitrogen consists of two positive nuclei of charge 7ϵ separated $9·1 \times 10^{-9}$ cm. from each other. Near each nucleus are two rings, an inner ring of very small radius containing two electrons, and an outer, bivalent ring of radius $8·05 \times 10^{-9}$ cm. containing ten electrons. The plane of the outer ring cuts the molecule symmetrically in two. This molecular model corresponds with an atomic model in which a univalent inner ring of two electrons encircles a nucleus, and concentric with this there is a bivalent outer ring of five electrons. The oxygen molecular model consists of two nuclei of charge 8ϵ, two inner rings each containing two electrons and an outer bivalent ring of twelve electrons. The oxygen atom model consists of an inner univalent ring of two electrons and a bivalent outer ring of six electrons.

J. F. S.

Distribution of Two Kinds of Atoms in the Regular Frankenheim-Bravais Space Lattices. G. Tammann (*Nachr. Ges. Wiss. Göttingen*, 1918, 190—234; from *Chem. Zentr.*, 1919, i, 781—782).—Experiments on the reaction limits of mixed crystals show that the distribution of two kinds of atoms in a stable complex cannot occur irregularly in accordance with the laws of probability. In the formation of mixed crystals, a distribution occurs with the help of diffusion. After slow cooling of a mixed crystal in which the orderly arrangement of the different atoms has taken place at a higher temperature, a very regular distribution without appreciable variation can permanently persist, as is shown by the fact that the reaction limits are not displaced in the direction of greater concentration of the less active atom

after weeks or months. The crystalline form of well-defined mixed crystals does not differ from that of their components. In similar directions, the properties of mixed crystals are generally as equivalent to one another as in unmixed crystals. Exceptions are found to this rule, however, since in many cases double refraction has been observed in mixed crystals the components of which crystallise in the regular system. The distribution of the atoms is not definitely determined by the postulate of equivalent directions, but becomes definite when the conception of intimate admixture (which occurs at the temperature of rapid diffusion of the atoms) is also introduced. The requirement may be summarised in the statement that accumulations of similar atoms do not occur on the perpendiculars and that the number of lattice perpendiculars of a group is at a minimum. This type of distribution of atom is termed "normal." Two other types of distribution are of interest: (1) such as fulfil the requirements of symmetry but not of most intimate mixture, and (2) those which, whilst having intimate mixture, possess a degree of symmetry lower than that required by the type of lattice. The normal type is the most stable, since, in it, only transitory local changes can be caused by diffusion. Mixed crystals of the third type cannot be optically distinguished from normal crystals into which they should be transformed by rise in temperature. Frankenheim and Bravais have distinguished three types of regular space lattices; the cube, the corners of which are occupied by atoms, is the lattice element of the first, the 8-point lattice. If an atom is considered to be placed in the centre of the cube, the 9-point lattice is obtained, whilst the 14-point lattice is derived by the introduction of atoms at the centres of the faces of the cube in the 8-point lattice. There are two possible ways of determining the normal distribution in these lattices. Either one can choose the corresponding groups in certain directions from the series of groups of lattice perpendiculars, the similar groupings round which are prescribed by the requisite relationships of mixture, or one can dissect the lattices into component lattices. The latter method has marked advantages, but the mixture relationships are thereby definitely fixed. The distribution of the atoms in the various lattices is discussed. The reaction limits of mixed crystals have been studied in such series which have a normal arrangement of atoms. The solubility of hydrogen in palladium, and the limit of this solubility, indicates an instance in which the agent penetrates the lattice; an atomistic explanation of this limit is given on the assumption of a 14-point lattice. In the cases of series of mixed crystals of gold with copper or silver, the reagents do not penetrate the mixed crystals. The atomistic constitution is very closely connected with the different action limits. The differing action limits of different reagents which, for example, withdraw the copper from the mixed crystal, are explained on the assumption that the agents require differing numbers of copper atoms for their action which are only to be found in differing directions. H. W.

Valency Isomerism. J. V. Dubsky (*Chem. Weekblad*, 1919, **16**, 984—995).—A summary and discussion of some recently investigated cases of valency isomerism. W. S. M.

Physical Nature of Valency. W. Kossel (*Naturwiss.*, 1919, **7**, 339—345, 360—366; from *Chem. Zentr.*, 1919, iii, 83—86).—The behaviour of carbon in exhibiting a constant valency, previously considered as particularly simple and typical, must be regarded as exceptional when compared with the majority of elements in which the polar character is marked. In general, a distinction must be made between heteropolar and homopolar linkings. The former not only occur more commonly, but also correspond with the best defined characteristics of valency. The double molecules of elementary gases may be regarded as examples of the latter, and in this connexion the polar neutrality of carbon appears exceptional. The position of carbon among the elements indicates its quadrivalency, but this should be positive from analogy with the preceding elements and negative as judged from its successors. Also, the maximum co-ordination number of carbon and its neighbours is four. A certain stability is thereby caused which is not generally associated with homopolar character, and since similar external conditions are only otherwise associated with silicon (and even then not in the same degree), carbon occupies an almost unique position, which, though rendering it able to form an exceptional number of compounds, makes it quite unsuitable for a general study of valency. The electro-chemical valency theory of Berzelius has been repressed, not only by reason of the preponderating developments of the chemistry of carbon, but also by the apparent necessity of attributing an opposite charge to the two similar portions of a molecule, such as that of hydrogen; this difficulty is removed by the conception of electrons. The electric forces need no longer be regarded as proceeding from the atom as a whole. The individual components exercise attractive force towards one another, and may thus cause the union of atoms without leaving the latter and causing them to be discharged, or certain components, symmetrically arranged, may form a uniting bridge between the atoms. The gradual transition from this type of union to that in which the atoms appear as polar (in which the components have passed from one atom to another and the atom as a whole may be regarded as discharged) is perfectly natural. Bohr's hydrogen model represents the most complete representation of a homopolar molecule. The author gives a historical review of the attempts made since the introduction of the conception of electrons to represent atomic structure and valency with the aid of the quantum theory, and discusses the models of Stark, J. J. Thomson, and Rutherford, together with Bohr's modification of the latter. Since the latter assumes that the electrons of an atom invariably follow their paths in regular order, which is necessary for equilibrium, and since their motion must act externally, as if the charge distributed itself uniformly over the path, the

complete model must appear externally as a symmetrical form, the action of which, after reception or expulsion of electrons, must be governed by the total charge which it has received as a whole. The action of such charges can be calculated with considerable certainty on the assumption that the charges are uniformly distributed, that is, that the resultant charge acts at the centre. A particularly simple electrostatic theory of valency of heteropolar compounds is thus obtained. The process of the union of atoms occurs in two stages, the first consisting in the exchange of electrons, the second in the union of ions. The meaning of the regular course of polar valency activity in the periodic system is discussed. For example, the potassium atom has 19 electrons, which are diminished to 18 when it becomes ionised. With chlorine, on the other hand, the number of electrons is increased from 17 to 18 when the free element becomes ionised. Inactive argon has itself 18 electrons, and this number is also attained by multivalent elements, more distant from argon in the system, in the ionised state. It may be generally stated that the strongly polar elements surrounding the rare gases attain the same number of electrons as the latter when combined. The arrangements of electrons in the rare gases are the most stable, and are the only ones which permit the reception of electrons.

Amongst elements of the type of the rare gases, the common arrangement of electrons occasions repelling forces when the atoms approach one another. On the other hand, alteration in valency is attributed to alteration in the charge of the nucleus, which, in conjunction with the constancy in number of the electrons, imparts a varying total charge to the atoms. The properties of such simple atomic models, having a central charge surrounded by an impenetrable zone, can readily be calculated. Although the atoms, in consequence of integral increase in the total charge, unite in integral ratios, there is nothing in the nature of the model which points to the exercise of special forces in spatially fixed directions, as is indicated by the usual structural formulæ. Actually, atoms frequently exhibit combining powers which cannot be classed with the definite valencies; Werner's complex compounds provide the best known example of this type. A number which represents the degree of charge, and which is identical with the number of chief valencies, is peculiar to each atom of a polar compound. A neutral molecule, for example, must contain equal charges of either sign; two such molecules, however, may yield a third neutral molecule with the help of the attractive forces of their disengaged charges of opposite sign. On the other hand, the degree of charging determines the affinity of one atom for another, and the work necessary to separate them. This work governs the frequency of separation (degree of dissociation of the compound), and the power of a substance to yield ions depends, therefore, on the valency of the atoms. Elements, such as gold, which possess high valency and small volume, are particularly adapted to function as nuclei in complex compounds, and this property is common to all elements

which have one or both of these characteristics. This point of view is further illustrated by reference to the hydrogen compounds of the elements at the negative end of the periodic table. The acidity decreases from fluorine through oxygen to nitrogen in proportion as the hydrogen is more firmly united in consequence of increased nuclear charge. Similarly, in the groups of the periodic system, hydrogen should be progressively less firmly retained as the atomic volume of the second element increases; this is the case in the sixth, but not in the seventh, group. Thirdly, every atom should detach hydrogen ions from electrostatically weaker atoms. Thus the $\overline{\overline{O}}$ of water removes hydrogen ions from compounds of those elements which are placed to the right and below it in the periodic classification. On the other hand, the $\overline{\overline{N}}$ of NH_3 is more potent than $\overline{\overline{O}}$, and therefore removes hydrogen ions from water to form $\overline{N\overset{+}{H}}$ and $\overline{O\overset{-}{H}}$.

The behaviour of elements exhibiting various degrees of oxidation, or, more exactly, the maximum degree of hydroxylation of such oxides, affords further possibilities of application for the theory. Such compounds can decompose in two ways, yielding either hydroxyl or hydrogen ions. If a definite assumption is made with regard to atomic radius, the work involved in the dissociation of such compounds within the periodic system can be exactly calculated. Highly charged ions are too unstable to be found free in aqueous solution. Electrostatic attractive forces are capable of representing the forces of valency with such exactitude that it appears doubtful whether other forces are involved. A complete representation of the atoms is necessary if the forces in polar molecules are to be exactly ascertained and the dissociation tensions and heats are to be calculated, and, more particularly, if the laws governing homopolar compounds are to be investigated. The experimental methods consist in observations of the natural vibrations of the atoms (Röntgen and optical spectra, etc.), and of the forced vibrations of the electrons of the atoms (refraction and dispersion of light, dispersal of Röntgen rays). The complete representation of the forces which determine the valency action of atoms involves, not only electrostatic, but also electromagnetic, principles, and, in a subsidiary degree, the action quantum.

H. W.

Alignment Chart for the Solution of Molecular Weight and Vapour Density Problems. Leslie J. Harris (*Chem. News*, 1919, **119**, 49—51).—A chart, on the principle of the slide rule, is described whereby from weight and volume measurements the vapour density or molecular weight of a gas may be directly read.

J. F. S.

Automatic Extraction Apparatus. Joseph Tcherniac (T., 1919, **115**, 1090—1092).

Inorganic Chemistry.

Manufacture of Metal Chlorides. William Heap and Edgar Newbery (Brit. Pat., 130626).—The anhydrous chlorides of aluminium, magnesium, cerium, and other rare earths are obtained by treating the oxides, or a salt with a weak acid, such as the carbonate or oxalate, with carbonyl chloride at a suitable temperature. With alumina, a temperature of 350—400° is required; magnesia, 500—600°; and cerium oxide, 650°. The carbonyl chloride may be replaced by a mixture of carbon monoxide and chlorine, passed over a catalyst, such as animal charcoal, before reaching the metallic oxide, and the process may also be used for dehydrating hydrated chlorides of the above-mentioned metals. Although the patent only applies to the above metals, the reaction is general, and is particularly useful also for the preparation of anhydrous calcium and ferric chlorides. G. F. M.

Preparation of Hydrobromic Acid, using Potassium Bromide, Sulphuric Acid, and Stannous Chloride. Alwyn Pickles (*Chem. News*, 1919, **119**, 89).—To 25 c.c. of a solution of potassium bromide (90 grams of the salt in 150 c.c. of solution) were added 0·2 gram of stannous chloride and 3·4 c.c. of concentrated sulphuric acid; by distillation at 120—127°, a solution of hydrogen bromide was obtained which was free from tin and almost free from hydrogen chloride, the yield being 95%. If a larger quantity of stannous chloride is used, the distillate contains tin and hydrogen chloride. C. S.

Compounds of Arsenious Acid with Iodides of Multivalent Metals. R. F. Weinland and Paul Gruhl (*Arch. Pharm.*, 1917, **255**, 467—481).—The iodides of a number of bivalent light and heavy metals, as well as that of aluminium, form compounds with arsenious acid. When the moderately concentrated solution of the iodide, saturated in the hot with arsenious acid, is allowed to cool, the compound, sometimes together with a little free arsenious acid, separates in small crystals, which have no distinct crystalline form, or consist of well-formed, microscopic, hexagonal leaflets. The following compounds have been thus prepared: $GlI_2,3As_2O_3,8H_2O$, $Mg(\text{or Ca or Sr})I_2,3As_2O_3,12H_2O$, $BaI_2,3As_2O_3,9H_2O$, $ZnI_2,3As_2O_3,10H_2O$, $Mn(\text{or Fe or Co})I_2,4As_2O_3,12H_2O$, $NiI_2,4As_2O_3,10H_2O$, $AlI_3,6As_2O_3,18(?)H_2O$, and $LiI,2As_2O_3,3H_2O$. In general, the characters of the iodides are suppressed in these compounds, which resemble more the arsenites of the metals. In dry air they are moderately stable, but gradually become yellow or brown, with conversion of the arsenious to arsenic acid in the case of the alkaline earth compounds and oxidation of the metal with

the ferrous and manganous compounds; this decomposition is most rapid with the ferrous, manganous, and aluminium compounds, and may be accelerated by heating the compounds in the air. In a vacuum over sulphuric acid or in a current of hydrogen at 100°, the water of crystallisation is completely lost with only minimal decomposition of the compounds; part of the water is reabsorbed from the air. The cobalt salt is pale red, the nickel salt pale green, and the rest colourless. With the exception of that of magnesium, these compounds are sparingly soluble in water, and when heated with water they appear to undergo partial dissociation into the iodides and arsenious acid. When the solutions are evaporated, salts richer in arsenious acid, but of no simple formula, separate out, owing to the fact that the iodide is not in excess as it is in the solutions from which the compounds are originally deposited.

The constitution of the compounds is discussed, and the conclusion is drawn that the anion is formed by union of the molecules of arsenious anhydride with the iodine atom or atoms, whilst the metal forms the cation.

Solutions of chromic and stannous hydroxides in hydriodic acid take up arsenious anhydride, but complete decomposition occurs on evaporation.

Compounds of antimony trioxide similar to the above were unobtainable in aqueous solution, but this oxide dissolves in fused potassium iodide, giving the amber-yellow, transparent, crystalline compound, $8Sb_2O_3,K_2O,2KI$.

Arsenic trisulphide is insoluble in potassium iodide solution, even on boiling, and solutions of thioarsenites in potassium iodide solution fail to give arsenic trisulphide compounds analogous to those of arsenious anhydride. T. H. P.

Freezing of Silicic Acid Coagula and the Problem of the Hydrates of Silica. I. and II. B. L. Vanzetti (*Atti R. Ist. Veneto Sci.*, 1915—1916, **75**, 261—266; 1916—1917, **76**, 287—292).—The author describes results of experiments following up the work of G. Bruni (*Rend. soc. chim. Rom.*, 1905, **3**, 2) on the comparison of the dehydration of silicic acid gels by evaporation and freezing. It is found that with gels varying in initial concentration from 3 to 10% of silica frozen at about −20°, the final ratio of water to silica depends principally on the initial concentration being higher the more water was initially present. Substantially the same conditions were reached for dehydration by freezing at −17° as for drying in air at constant temperature and humidity. A marked influence in the age of the gels was observed, similar to that noted by van Bemmelen, in that with older gels freezing produced a much more advanced dehydration. The results are regarded as in agreement with the absorption theory and as giving no support to the view that specific hydrates of silica are concerned.

In the second paper further experiments are detailed in which

both the time of drying was greatly prolonged at normal temperature (15°) and the degree of cooling greatly increased for the freezing experiments, mixtures of carbon dioxide and acetone, and liquid air being used. The results confirm the previous ones for shorter periods and higher temperatures. As before, it was found that the final composition depends entirely on the initial concentration and the age of the gel, and not at all on the temperature of freezing. This independence of the gel state of temperatures down to −200° is regarded as contributing a new datum to the granular theory of the gel constitution. Whilst the status of the last traces of water not removed by freezing cannot yet be decided, the results illustrate the relationship of silicon and carbon and their relative positions in Mendeléev's system; in both cases, in the process of evaporation of water, there is manifest a tendency to the separation of the anhydride passing to conditions of maximal stability, in the one case as solid, in the other as gas.

CHEMICAL ABSTRACTS.

Selective Combustion of Carbon Monoxide in Hydrogen. ERIC KEIGHTLEY RIDEAL (T., 1919, **115**, 993—1006).

Sodium Hypochlorite. MALCOLM PERCIVAL APPLEBEY (T., 1919, **115**, 1106—1109).

Action of Copper on Sodium Nitrite. WALTER PETERS (*Zeitsch. anorg. Chem.*, 1919, **107**, 313—316).—Experiments are described in which metallic copper was warmed at 60° with a 5% aqueous solution of sodium nitrite, in presence of carbon dioxide, air being excluded from the reaction vessel. Decomposition of the nitrite occurred with evolution of nitrous gases. Analysis of the gas and of the residual solution showed that the former contained nitrous and nitric oxides whilst the latter contained nitrate. The decomposition of the nitrite is not catalytic, but chemical, involving simultaneous oxidation and reduction. It has not been found possible to represent the reaction by an equation. Other metals, such as lead, iron (filings), and cobalt dissolve in the nitrite solution, but without evolution of gas. In the case of cobalt, sodium cobaltinitrite is formed in solution. E. H. R.

Manufacture of Strontium Peroxide. JAMES BUCHANAN PIERCE, jun. (Brit. Pat., 130840).—Strontium oxide combines directly with oxygen under a pressure of 105—126 kilos. per sq. cm. at a temperature of 400—500°. The resulting peroxide contains over 85% of SrO_2, and resembles barium peroxide in physical properties. G. F. M.

Anhydrous Phosphates, Arsenates, and Vanadates of Lead. M. AMADORI (*Atti R. Ist. Veneto Sci.*, 1916—1917, **76**, 419—433).—Thermal studies of the systems PbO–P_2O_5, PbO–As_2O_5, and PbO–V_2O_5 are described. The investigation was suggested by the analogy of these compounds to the calcium derivatives as in Thomas slag, and in the work of Kroll. Formation of compounds with lead

oxide occurs in the diminishing order P_2O_5, As_2O_5, and V_2O_5. The PbO content is upwards of 66·66% mol. The phosphates, arsenates, and vanadates are pyro- (as P_2O_5,2PbO), ortho- (as P_2O_5,3PbO), and octa- (as P_2O_5,8PbO). In addition, there is an anorthophosphate, $2P_2O_5$,5PbO, and a metaphosphate, P_2O_5,PbO. A tetra-arsenate, As_2O_5,4PbO, is probably also formed.

CHEMICAL ABSTRACTS.

Thallium–Tin Alloys. PAUL FUCHS (*Zeitsch. anorg. Chem.*, 1919, **107**, 308—312).—A thermal investigation of the alloys of thallium and tin has shown the existence of a eutectic point at 166° with 30 at. per cent. of thallium. The eutectic horizontal extends from 0 to 73 at. per cent. of thallium; with a greater proportion of thallium the alloy forms homogeneous, mixed crystals. Alloys with less than 73% of thallium show on cooling, in addition to the arrest point at the eutectic temperature, a second arrest at 144·5°. This arrest point represents the transition point of thallium, lowered through the influence of the tin from about 231°, the transition point of pure thallium. In the mixed crystal region, that is, from 73 to 100% of thallium, the transition point is lowered approximately in proportion to the amount of tin present. The arrest point at 144·5° is the transition point of saturated mixed crystals containing 73 at. per cent. of thallium. E. H. R.

Aluminium and a Double Salt. E. RATTENBURY HODGES (*Chem. News*, 1919, **119**, 64).—When aluminium foil is submitted to the action of dilute nitric acid for seven to eight weeks it dissolves, and on evaporating the solution a light grey, colloidal mass containing some free acid is obtained. This solid is nearly all hydroxide, and on exposure to a moist atmosphere is completely converted into hydroxide. J. F. S.

Ternary Alloys of Aluminium with Magnesium and Copper. RUDOLF VOGEL (*Zeitsch. anorg. Chem.*, 1919, **107**, 265—307).—A thermal and microscopical study has been made of ternary aluminium–magnesium–copper alloys containing up to 55% of magnesium and 54% of copper, and from the results the solid, triangular equilibrium diagram limited by the phases Al, Al_2Cu, and Al_3Mg_4 has been constructed. It is known that, with copper, aluminium forms mixed crystals containing up to 4% of copper, whilst with a greater proportion of copper an eutectic of these mixed crystals and the compound Al_2Cu is formed. It is now found that aluminium also forms mixed crystals with magnesium with a maximum magnesium content of 6%. With more than this proportion of magnesium a second mixed crystal constituent appears containing the compound Al_3Mg_4. This constituent being hard and brittle, the presence of more than 6% of magnesium in these alloys is likely to be disadvantageous.

The compositions of the ternary alloys examined were so chosen that seven sections of the Al–Al_2Cu–Al_3Mg_4 diagram could be constructed, and from them the complete three dimensional diagram

deduced. These sections and the complete diagram are fully discussed. The following constituents occur in the ternary alloys: ternary mixed crystals of the three elements, ternary mixed crystals containing Al_2Cu, a ternary compound, Al_6Mg_4Cu, and binary Al–Mg mixed crystals. When a polished section of a ternary alloy is etched with concentrated nitric acid, the mixed crystals containing Al_2Cu are blackened in about half a minute, the crystals of the ternary compound become brown to black much more slowly, the mixed crystals of the series containing more than 6% of magnesium become yellow, whilst the ternary mixed crystals rich in aluminium remain bright. On adding a drop of water to the nitric acid the black Al_2Cu mixed crystals become bright red owing to the deposition of copper, whilst the ternary compound rapidly blackens. A number of photomicrographs of different alloys are reproduced. The ternary compound forms crystals which are hard and brittle; consequently, it is an undesirable constituent.

Binary alloys of aluminium with 1—10% of magnesium show a secondary arrest point at 584°, with 2—5% of copper at 513—529°, and with both magnesium and copper present, between 557° and 564°. It appears probable that this thermal effect is due to an allotropic change of the aluminium induced or accelerated by the foreign constituent. The aluminium used contained some iron and silicon, but no microscopic evidence of the formation of an eutectic with either of these elements could be detected. A similar arrest point was observed by Gwyer (A., 1908, ii, 284) with aluminium alloys containing nickel and cobalt. The possibility of allotropic change of the aluminium does not explain, however, the increase in tensile strength which aluminium alloys containing magnesium and copper undergo after heating to about 500° and cooling to the ordinary temperature. This phenomenon cannot yet be explained.

E. H. R.

Regularities in the Chemical Action of Gases on Iron and its Compounds with Non-metals at High Temperatures. Friedrich Schmitz (*Stahl u. Eisen*, 1919, **39**, 373—381, 406—413; from *Chem. Zentr.*, 1919, iii, 6—7).—When pure hydrogen is passed over strongly heated technical iron or is blown through molten iron (pig iron, ferrous alloys, steel), the non-metals which are present in the free or combined state are converted into the corresponding gaseous hydrides; the behaviour of pure non-metals (carbon, silicon, arsenic) is similar. The hydrides dissociate to some extent at the high temperature, and the nascent hydrogen, in the absence of oxygen, can reduce silica, even at 700°, to silicon hydride. The salts of iron are converted at elevated temperature in the presence of hydrogen into iron and free acids. If, on the other hand, iron is ignited in a gaseous hydride, hydrogen is liberated, which, in part, diffuses into the iron, and the non-metal or acid radicle combines with the iron. Under definite external conditions of temperature and pressure, an equilibrium is set up for each non-metal; a definite relationship between hydrogen and non-metallic hydride is established, at which neither cementation nor

tempering occurs. In an atmosphere of pure hydrogen or nitrogen at an elevated temperature, both carbon and silicon can diffuse into solid iron without previous formation of gaseous substances.

Compounds of iron, oxygen, and the corresponding non-metal are formed when metalloid compounds of iron are ignited in pure oxygen. If these compounds contain carbon, sulphur, or arsenic, they decompose at a higher temperature, yielding ferric or ferrous oxide and the gaseous oxide of the metalloid. If iron is ignited in a gaseous compound of a metalloid, which can be replaced by hydrogen, and oxygen, a compound of iron, oxygen, and the non-metal or hydrogen is first produced. Such compounds, which contain phosphorus and silicon, are stable when the temperature is raised; those, however, in which carbon, sulphur, arsenic, and hydrogen are present decompose at a slightly increased temperature, giving ferric or ferrous oxide and gaseous compounds of the non-metal or hydrogen with oxygen. Nitrogen has no action on non-metals present in solid or liquid iron. The diminution in the carbon content, frequently observed after ignition in nitrogen, becomes progressively smaller as greater care is taken to free the nitrogen from oxygen and gases containing oxygen. H. W.

Alloys of Iron and Nickel Deposited Electrolytically. P. Benvenuti (*Atti R. Ist. Veneto Sci.*, 1916, **76**, 453—477).—The author reviews the work of Bruni and Amadori and other experimenters in depositing alloys containing nickel and iron, and describes his own investigations to discover the best conditions for producing the deposit. The composition of the bath and its relation to the composition of the alloy deposited is discussed from his data. The physical structure of Ni–Fe alloys of different composition is shown in photomicrographs. Tables show the atomic % of iron varying from 2 to 97, the duration of the electrolysis, the weight of the alloy deposited, and the weight and % of the iron contained in the deposit. Iron in the alloy was estimated volumetrically by permanganate. The cell was maintained at 25° (±0·1°) in a thermostat and platinum electrodes were used. Each electrolysis lasted about eight hours. Current was maintained at 25 milliamp. and the current density at the cathode was 0·5 ampere per sq. dm. The two metals may be easily deposited simultaneously. An ammonium tartrate bath with less than 73% or more than 75% of iron gives deposits containing more and less iron respectively than is contained in the solutions. A bath containing 26% of nickel and 74% of iron deposits an alloy of the same composition, which is that of stable equilibrium at ordinary temperature and pressure, and is also that of the eutectic alloy, and that of the solid saturated solution, the meteoric mineral tænite, solid solution of iron in nickel, and of kamazite, solid solution of nickel in iron. The deposits by the current are such as to indicate in the deposits the co-existence of two types of saturated solid solution. The study of the electrolytic potential supports the hypothesis proposed above. The micrographic study of the deposits furnishes evidence of the presence of two structures in all the alloys, what-

ever may be their composition. It is probable that in the course of their deposition, the alloys Fe–Ni electrolytically tend, without reuniting, towards the state of equilibrium of nickeliferous iron in the original meteorites. CHEMICAL ABSTRACTS.

Meteoric Nickel-Iron and the Polymorphism of Carbon-Iron. G. TAMMANN (*Nachr. Ges. Wiss. Göttingen*, 1918, 258—266; from *Chem. Zentr.*, 1919, i, 806—807).—According to Osmond and Cortaud (A., 1904, ii, 135), tænite is to be regarded as a particular phase, since it is sharply separated from kamacite, particularly after being etched. The author, however, is more inclined to regard it as a deposit in kamacite rather than to consider that the substances represent two phases in equilibrium with one another. According to the recent experiences on the reaction limits of chemical agents on mixed crystals, two portions of a conglomerate which show widely differing behaviour towards reagents are not necessarily to be regarded as distinct phases. The determination of limits of action in technical nickel–iron is rendered impossible by the presence of oxygen. It appears questionable whether tænite itself is homogeneous. If the latter is not regarded as a separate phase, there is no difficulty in interpreting the meteoric structure on the basis of the known equilibrium diagrams of nickel steels, and the meteoric structure may be assumed to be due to the crystallisation of the respective molten masses. In this case there must not be expected the normal, stable distribution of the nickel and iron atoms, such as occurs in the space lattice of technically homogenised nickel irons, but a different, unstable arrangement. The structure of meteoric iron shows the manner in which the distribution of both kinds of atoms in kamacite differs from the normal. The atoms of the meteorite, like those of technical nickel–iron, probably occupy the points of a 14-point space lattice, the element of which is the cube with atoms at the corners and in the middle of the sides; the latter occupy the corners of an inscribed octahedron. The difference between kamacite and technical nickel–iron may be explained by assuming that, in the former, the lattice perpendiculars parallel to the edges of the octahedron are occupied by an abnormal number of nickel atoms. It is admitted that a form which is unstable when heated may be permanent when it has separated from the molten state. According to the author, therefore, kamacite is a mixed crystal in which the distribution of the nickel and iron atoms is not normal, but of lower symmetry, similar to the mixed crystals with double refraction. The tænite leaflets are layers orientated on the octahedral planes, whilst plessite represents portions richer in layers. Unstable forms, which are probably to be regarded as space lattice isomerides, are also found in carbon steels. H. W.

Monoclinic Double Selenates of the Cobalt Group. A. E. H. TUTTON (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 156—184).—Continuing the crystallographic investigation of the salts

of the series $R_2M(SeO_4)_2,6H_2O$, the author now reports the results of the examination of the four salts in which M is cobalt and R is potassium, rubidium, cæsium, and ammonium. As in the case of the corresponding double ferrous selenates (this vol., ii, 346), all four salts crystallise in the holohedral class of the monoclinic system and are isomorphous with the other members of the series. The relations between the four salts correspond exactly with those found in the case of the salts of the ferrous group.

Potassium cobalt selenate, $K_2Co(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7522:1:0{\cdot}5062$, $\beta=104°17'$, D_4^{20} 2·530, M.V. 208·6.

Rubidium cobalt selenate, $Rb_2Co(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7427:1:0{\cdot}5019$, $\beta=105°14'$, D_4^{20} 2·837, M.V. 218·49.

Cæsium cobalt selenate, $Cs_2Co(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7310:1:0{\cdot}4989$, $\beta=106°18'$, D_4^{20} 3·094, M.V. 230·73.

Ammonium cobalt selenate, $(NH_4)_2Co(SeO_4)_2,6H_2O$, $a:b:c=0{\cdot}7449:1:0{\cdot}5031$, $\beta=106°23'$, D_4^{20} 2·228, M.V. 218·1.

Comparing the molecular volumes of analogous double sulphates and selenates of the different groups which have been investigated, it is seen that the replacement of one atom of sulphur by one of selenium increases the molecular volume by a quantity varying only between the limits 6·0 to 6·8 units. In the simple alkali sulphates and selenates the increase is 6·5 to 6·8 units per atom substituted. The optical constants of the salts have been accurately determined.

E. H. R.

Action of Oxygen on the Precipitation of Metals from Cyanide Solutions. Oliver P. Watts (*Chem. Met. Eng.*, 1918, **18**, 652—653; from *Chem. Zentr.*, 1919, i, 811).—According to Crowe (*Chem. Met. Eng.*, 1918, **19**, 283), the precipitation of gold is caused by hydrogen liberated by the zinc, so that removal of dissolved air from the cyanide solution acts favourably, since it prevents the loss of reducing agent by oxidation. The author, on the other hand, is of opinion that the gold is directly precipitated from its solutions by zinc in the same manner as is copper from copper sulphate solution. The solution of zinc in sodium cyanide only differs from its solution in copper sulphate in that hydrogen is liberated in place of copper. The presence of oxygen is necessary for the rapid solution of zinc or other metals in cyanide solutions, whilst it has no influence on the solution of zinc in copper sulphate. Two simultaneous actions occur when zinc is placed in a dilute solution of cyanide containing gold. A portion of the zinc is dissolved by the double cyanide with precipitation of gold, whilst another portion is dissolved by the sodium cyanide with evolution of hydrogen; only the former action is useful in the separation of gold. For every gram of hydrogen evolved, 32·5 grams of zinc are dissolved without precipitation of gold, whilst, also, the excess of cyanide with which the zinc reacts is not profitably utilised. This undesired solution of zinc is limited by the content of oxygen or air, which oxidises the polarising deposit of hydrogen. Not only does dissolved air cause a loss of zinc, but it also diminishes the

yield by expediting the re-solution of the precipitated gold in the same manner as it promotes the solution of metals in the treatment of ores with cyanide solutions. H. W.

Mineralogical Chemistry.

Theory of Magmatic Mineral-forming Agents. JOHANN JAKOB (*Zeitsch. anorg. Chem.*, 1919, **106**, 229—267).—An important part in mineral and rock formation has undoubtedly been played by the gaseous and more or less easily volatile substances present in the magma. Among these mineral-forming agents water is by far the most important; other agents discussed include hydrogen sulphide, hydrogen fluoride, the oxides of carbon, sulphur dioxide, titanium dioxide, and a number of the less common metallic and non-metallic oxides. A precise definition of a mineral-forming agent cannot be given, but it must possess the property of forming additive compounds with other substances present in the fluid magma. These compounds are supposed to be of the co-ordinated type and generally to form mobile, complex ions. Through the interaction of these complex ions in the magma the different minerals are formed. For the purpose of discussion, the magma is considered as a highly concentrated solution of the other constituents in the mineral-forming agent; for example, in the case of water, as an aqueous solution. Hydrated forms of the different oxides present are probably produced, in which the elements can be supposed to exert the maximum co-ordinating power, with formation of such compounds as $[(H_2O)_2Si(OH{\cdot}OH)_4]H_4$ and $[Mg(OH)_2(OH_2)_4]$.

At the high temperature of the magma, water is comparatively highly dissociated, and the hydrogen and hydroxyl ions combine with the hydrated compounds to form complex hydrated ions, through the interaction of which the different minerals are formed. New formulæ of the co-ordinated type are suggested for some of the complex silicates. The same ideas are applied to the discussion of rock metamorphosis. E. H. R.

Chemistry of Coal. I. Action of Pyridine on the Coal Substance. WILLIAM A. BONE and REGINALD J. SARJANT (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 119—136).—Experiments on the solvent action of pyridine on coal have shown that the presence of oxygen has an important retarding action, varying with the nature of the coal, on the extraction process. This is due to the oxidation of the coal substance which may occur before or during the extraction. Previous oxygenation of the coal renders it much less susceptible to the solvent action of pyridine. The presence of water in the pyridine also has a retarding influence. To obtain concordant results

it is therefore necessary to exclude air, to use carefully dried and purified pyridine, and in addition to grind the coal to a standard mesh and to have a standard form of extraction apparatus. Such an apparatus is described in the present paper. The picolines extract about the same amount as pyridine, but, owing to their greater instability, they are less suitable as solvents. When the pyridine extract, which may amount to more than 30% by weight of the original coal, is again extracted with chloroform about 50% is dissolved. According to Clarke and Wheeler (T., 1913, **103**, 1704), the chloroform effects a complete separation of the resinic from the cellulosic constituents of the coal, but the analysis of the pyridine–chloroform extract does not warrant the view that it represents even an approximately pure coal resin. [See also *J. Soc. Chem. Ind.*, 1919, October.] E. H. R.

Relations between Tridymite and Cristobalite. C. N. Fenner (*J. Soc. Glass Tech.*, 1919, **3**, 116—125).—The author disputes the conclusion of Rees (*J. Soc. Glass Tech.*, 1918, **2**, 253), Scott (*ibid.*, 1918, **2**, Abs. 169), and Le Chatelier (A., 1917, ii, 97) that tridymite is more stable than cristobalite at temperatures above 1480°. He cites numerous experiments to the contrary, and states that in the course of a long series of experiments, no obvious loophole was left by which it was possible to escape the conclusions regarding the stability relations which have been drawn. At temperatures above 1470±10°, quartz, tridymite, and amorphous silica have repeatedly and unequivocally been converted into cristobalite; between 1470±10° and 870±10°, quartz, cristobalite, and amorphous silica have similarly been converted into tridymite; and below 870±10° tridymite, cristobalite, and amorphous silica have been converted into quartz. These relations have been confirmed again and again. Moreover, recent work by Ferguson and Merwin (A., 1918, ii, 362) has indicated that the melting point of tridymite is considerably lower than that of cristobalite. It follows necessarily from this observation that cristobalite is the high-temperature form. [See *J. Soc. Chem. Ind.*, 1919, 722A.] A. B. S.

Composition of Bornite. Austin F. Rogers (*Science, New York*, 1915, [N.S.], **42**, 386—388).—The formula proposed by Kraus and Goldsberry (A., 1914, ii, 570; compare Allen, A., 1916, ii, 391) is discussed. Fifty-nine published analyses are plotted on a triangular diagram; they all fall near the line $CuFeS_2$ to Cu_2S, with the greatest cluster near Cu_5FeS_4, and lower and upper limits near Cu_3FeS_3 and $Cu_{12}Fe_2S_9$. The most probable explanation of the variations in composition of bornite is that of a solid solution of Cu_2S in Cu_3FeS_3, the formula being written as $Cu_3FeS_3(Cu_2S)_x$. L. J. S.

Scapolite of Gem Quality from the Pegmatites of Madagascar. A. Lacroix (*Compt. rend.*, 1919, **169**, 261—264).—Transparent, yellow scapolite occurs as corroded and striated square prisms several cm. in length, together with beryl, euxenite, and monazite, in a potash-pegmatite at Tsarasaotra on the Tsibohaina

river. D 2·67. Optically uniaxial and negative with slight pleochroism, $\omega_{Na}=1·5698$, $\epsilon_{Na}=1·5490$, $\omega-\epsilon=0·0208$. It is rather harder (H $6\frac{1}{2}$) than ordinary scapolite and shows no cleavage, the fracture being conchoidal. Estimations of some of the more unusual constituents gave (compare this vol., ii, 163):

CO_2.	Cl.	F.	SO_3.	SrO.	FeO.	Fe_2O_3.
2·52—2·71	1·59	0·37	nil	0·09	0·90	0·11

Cut stones resemble certain beryls in appearance and in some of their characters; there is, however, a marked difference in the strength of the double refraction and in the hardness. L. J. S.

Analytical Chemistry.

Normal Temperature for the Standardisation of Chemical Apparatus, etc. Walter Block (*Chem. Zeit.*, 1919, **43**, 477—479).—The author discusses the subject regarding the temperature at which laboratory apparatus should be standardised, and considers that 20° would be more suitable and convenient than 15°, a temperature now usually taken as the normal in chemistry and physics. W. P. S.

Automatic Apparatus for Gas Analysis. Olof Rodhe (*Svensk. Kem. Tidskr.*, 1919, **31**, 5—14).—The apparatus automatically estimates and records by means of a kymograph the relative amounts of oxygen, carbon dioxide, carbon monoxide, hydrogen, methane, or other constituent in a gas. It is constructed on the principle of a train of absorption, combustion, and measuring units without taps. One or more aggregates may be used and the flow of gas may be shunted from one to another, depending on the constituent considered significant in the control work, for example, carbon monoxide or hydrogen in a water-gas plant, carbon dioxide or oxygen in a lime or cement kiln, etc.

Chemical Abstracts.

Gas Burette. Paul Nicolardot and Gustave Prevot (*Ann. Falsif.*, 1919, **12**, 140—145).—The apparatus consists of a graduated tube, about 2 cm. in diameter, the upper part of which is widened out so as to form a cylinder of about 6 cm. in diameter and having a capacity three to four times that of the narrow tube; the wide portion of the burette is also graduated. The two ends of the burette are provided with taps. The capacity of the whole burette may be from 200 to 400 c.c. W. P. S.

Apparatus for the Collection of Gases in Spring Waters, etc. O. Hackl (*Chem. Zeit.*, 1919, **43**, 421—422).—A wide-mouthed bottle is closed with a rubber stopper through which pass the stem of a funnel and a short length of glass tubing.

To collect gases rising from a natural spring, the bottle is filled by immersing it in the water, then inverted so that the bubbles of gas are collected by the funnel and pass into the bottle, the water leaving the latter through the glass tube. When the bottle is full of gas, the stopper is removed while the bottle is still immersed in the water, and another stopper carrying two tubes is inserted; the outer ends of these tubes are closed by short lengths of rubber tubing carrying pinch-cocks. The gases are transferred to a Hempel apparatus by means of these tubes. A Bunsen collecting tube may also be used for the purpose, the end being closed with a rubber stopper carrying a funnel and side-tube; the stem of the funnel is provided with a length of rubber and glass tubing which extends below a constriction in the collecting tube just below the stopper. W. P. S.

The Boiling Point as a Criterion of Purity and a New Apparatus for its Determination without Correction for the Thermometer. Theodor Paul and Karl Schantz (*Arch. Pharm.*, 1919, **257**, 87—129).—The methods for the determination of the boiling point prescribed in the fifth edition of the German Pharmacopœia, when required for purposes of identification and as a means of controlling purity, have been critically examined. The latter method (distillation of a measured volume of the liquid under definite conditions) only gives a rough approximation of the true b. p., so that the data recorded in the Pharmacopœia do not generally coincide with the actual b. p.'s of the respective liquids even when these in other respects satisfy the pharmaceutical requirements. Further, the influences of variation in the barometric height and of the projecting thread of the thermometer are not taken into consideration.

The influence of common impurities on the b. p.'s of pharmaceutical preparations has been investigated. Addition of water lowers the b. p. of ethyl ether until it is present to the extent of 1·3%, after which no further depression occurs; ethyl alcohol, on the other hand, raises the b. p. of ethyl ether, and a specimen of the latter containing 1·15% of ethyl alcohol and 1·8% of water (by weight) has the same b. p. as pure ethyl ether. The depression of the b. p. of chloroform by addition of ethyl alcohol has been further studied: water produces a similar effect, but the quantitative relationships could not be studied by reason of peculiar condensation phenomena. The b. p. of ethyl bromide is depressed by the presence of ethyl alcohol or water, the effect of which when simultaneously present is additive. The presence of benzoic acid elevates the b. p. of benzaldehyde.

The boiling points for different barometric pressures, calculated according to the formula $t = t_0 - (t_0 + 273) \cdot c \cdot (760 - b)$, agree satisfactorily with the observed values.

A new apparatus is described which allows the determination of the boiling point of a liquid at constant composition and during fractional distillation. The vessel consists of a stout-walled test-tube about 18 cm. high and 20 mm. internal diameter which con-

tains a layer, 3 cm. high, of beads. So much liquid (about 15 c.c.) is used that its surface is about 3·5 cm. above the beads. A column is attached to the test-tube consisting of a vapour tube (23 cm. × 11 mm.) which is surrounded by a vapour jacket (20—22 cm. × 20 mm.), in which the thermometer is supported. The jacket and tube are sealed together about 14 cm. above the lower end of the tube. Immediately above the junction, a side-tube, which can be connected with a condenser, and a small bent tube, which is also sealed in to the lower portion of the vapour jacket and permits the condensed liquid to return to the still, are attached. The vessel is placed in the middle of an asbestos sheet in which a hole, 2 cm. in diameter, has been cut, the opening being closed from below by copper gauze. The asbestos sheet must be sufficiently large to prevent the radiant heat from the burner from affecting the thermometer. For liquids which boil above 100°, it is advisable to protect the boiling tube with an air-jacket. The thermometer is inserted in such a manner that the thread is completely surrounded by the vapour. The height of the flame is so adjusted that the liquid just boils vigorously. The b. p. is read when the thermometer does not show a variation greater than one-tenth of a degree during three minutes. By rotating the condenser through 180°, the apparatus may be used either for refluxing or for distillation. H. W.

Substitute for Hydrogen Sulphide Water. Bayer (*Pharm. Post*, 1918, 354; *Schweiz. Apoth. Ztg.*, 1919, **57**, 140).—Ten grams of sodium sulphide are dissolved in 50 c.c. of water + 50 c.c. of glycerol. No special apparatus is required.

Chemical Abstracts.

Stabilising Normal Alkali Solution. Winkler (*Pharm. Post*, 1918, 354; *Schweiz. Apoth. Ztg.*, 1919, **57**, 140).—The absorption of carbon dioxide by *N*-alkali may be reduced to a minimum by replacing 30% of the water used by 30% of glycerol. This also prevents the sticking of glass stoppers.

Chemical Abstracts.

Conditions for Obtaining Pure Sodium Carbonate for Standardising Acid and Applicability of Crystallised Oxalic Acid in place of the Anhydrous Acid as a Titration Standard. Hermann Kunz-Krause and Rudolf Richter (*Arch. Pharm.*, 1917, **255**, 540—549).—If stirred with a platinum wire, sodium hydrogen carbonate is converted quantitatively into sodium carbonate at 250°. Microcrystalline oxalic acid ($+2H_2O$) may be used for the direct preparation of standard acid; its solutions keep their titre if protected from the light. [See *J. Soc. Chem. Ind.*, 1919, October.] T. H. P.

Liquid Ammonia-Sodium Method for [Estimating Halogens in Organic Compounds, the Formation of Cyanide and the Method of Removing [it] from the Solution. Charles William Clifford (*J. Amer. Chem. Soc.*, 1919, **41**, 1051—1060).—This method of estimating halogens in organic com-

pounds, due to Chablay (A., 1914, i, 918), consists in adding liquid ammonia to a small quantity of the substance in a Dewar vessel, and then metallic sodium until a permanent blue colour is produced. The halogen is thereby converted into the sodium haloid. The excess of ammonia is allowed to evaporate, and the excess of sodium is removed by treatment with alcohol. The residue is dissolved in water acidified with nitric acid, treated with excess of standard silver nitrate, and the excess of silver titrated with sodium thiocyanate. This reaction has been investigated as to its trustworthiness. It is found that in many cases cyanide is also formed, and consequently the procedure as outlined above cannot, in many cases, be carried out without the possibility of error. On acidifying, only a portion of the hydrocyanic acid which may have been formed is expelled. At best, the decomposition of silver cyanide and elimination of cyanide by boiling in diluted nitric acid are only approximately quantitative. The percentage of cyanide formed is not a constant for each substance under the conditions of analysis. Treatment with sodium in liquid ammonia completely removes any halogen present in organic compounds, and the resulting haloid is separated quantitatively from any cyanide present by acidifying the solution with acetic acid and boiling. J. F. S.

Adaptation of the Mohr Volumetric Method to the General Estimation of Chlorine. Lester Yoder (*J. Ind. Eng. Chem.*, 1919, **11**, 755).—The following procedure is recommended for the estimation of chlorine in organic substances. A suitable quantity of the sample is treated with 5 c.c. of 30% calcium acetate solution and sufficient water to form a moist mass, the mixture is evaporated to dryness, and incinerated below 450°. The cooled residue is moistened with a few c.c. of 10% ferric acetate solution, again dried, and ignited below 450°. The residue is dissolved in water, the solution filtered, the filter washed with hot water, the filtrate evaporated to dryness, and this residue dissolved in a small quantity of water. After the addition of a few drops of potassium chromate solution, the chloride is titrated with standardised silver nitrate solution. The calcium acetate fixes free chlorine, precipitates carbonates, and neutralises the filtrate; the ferric acetate precipitates phosphates, and the excess is converted into insoluble ferric oxide during the ignition. W. P. S.

Simplification of Kjeldahl's Method in Clinical Chemistry. E. Pittarelli (*Riv. crit. clin. med.*, 1919; from *J. Pharm. Chim.*, 1919, [vii], **20**, 32—34).—To estimate nitrogen in urine, 1 c.c. of a 10% solution of the sample is digested with 2 c.c. of sulphuric acid and one drop of phenol, a small quantity of potassium persulphate being added towards the end of the reaction. The mixture is then neutralised, treated with 10 c.c. of a mixture of three volumes of saturated sodium hydrogen carbonate solution and one volume of saturated mercuric chloride solution, the whole

diluted to 250 c.c., and the turbidity compared with that obtained with a known quantity of ammonia. W. P. S.

Systematic Procedure for the Detection of Acids of Group I. Louis J. Curtman and David Hart (*Chem. News*, 1919, **119**, 25—29, 37—40).—A scheme is proposed by means of which the acids of group I may be systematically detected and the relative amounts approximately estimated. The chief steps in the scheme are (*a*) a preliminary precipitation of all the acids of group I with a mixture of barium and calcium chlorides, (*b*) treatment of the precipitate with hydrochloric acid to dissolve all but the sulphate, (*c*) oxidation with hydrogen peroxide to convert sulphite into sulphate and precipitation of the latter with barium chloride, (*d*) removal of barium from the solution with ammonium sulphate, (*e*) separation of fluoride, arsenate, and phosphate from borate and tartrate in alkaline solution in the presence of sufficient ammonium salts, (*f*) removal of oxalate and fluoride from arsenate and phosphate in an acetic acid solution containing an excess of calcium ions, (*g*) reduction of arsenate to arsenite with sulphur dioxide and separation from phosphate by hydrogen sulphide in hydrochloric acid solution, (*h*) separate tests for carbonates and chromates, and (*i*) separate tests for the determination of the state of oxidation of the arsenic. Very full details of the effect of the various acids on one another in the several stages of the separation are given, and by means of these the method is shown to be trustworthy. J. F. S.

Influence of Temporary Hardness on the Estimation of Chlorides in Water. W. Herbig (*Zeitsch. angew. Chem.*, 1919, **32**, 216).—The temporary hardness of water is without influence on the estimation of chlorides by Mohr's method, and consequently the procedure adopted by Lombard (A., 1913, ii, 1068) is unnecessary. W. P. S.

Rapid Estimation of Nitric Acid. Lucien Maugé (*L'Ind. chimique*, 1918, **8**, 255—256; from *Chem. Zentr.*, 1919, ii, 720).—When nitric acid is added to a solution of ferrous sulphate acidified with sulphuric acid, oxidation of a portion of the salt occurs, accompanied by formation of nitric oxide, which yields the intensely brown additive compound with the excess of ferrous sulphate; on further addition of nitric acid, the colour disappears as soon as the ferrous sulphate is completely oxidised: $6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$. The discharge of the colour is sufficiently sharp for the process to be applied to the volumetric estimation of nitric acid. The solution of ferrous sulphate contains 66·66 grams $FeSO_4,7H_2O$ per litre, and is standardised by permanganate; 10 c.c. of this solution are heated with 50 c.c. of sulphuric acid (60—66 Bé.) and titrated with the nitric acid under investigation until decolorised. H. W.

Estimation of Phosphoric Acid as Magnesium Pyrophosphate. D. Balareff (*Zeitsch. anorg. Chem.*, 1919, **106**, 268—280).—In the estimation of phosphoric acid by the double precipitation method, although trustworthy results are obtained, the ignited precipitate is not pure, but contains excess of magnesium and too little phosphoric acid (A., 1918, ii, 406). Neubauer's method for the estimation of magnesium, in which a solution of phosphoric acid is added to the magnesium solution, gives high results when the ammonia is added quickly for the second precipitation, but when the ammonia is added slowly the results approximate to those obtained by Schmitz's method (*loc. cit.*). The use of an alkali phosphate in place of phosphoric acid causes the results to be high on account of the precipitation of alkali magnesium phosphate.

Further experiments on Schmitz's method for phosphoric acid have been made. In this method excess of magnesium chloride is added to the phosphate solution, together with a quantity of ammonium chloride. Sufficient ammonia is then added to the hot solution to cause precipitation as the solution cools. Although this method gives consistent results with widely varying conditions of concentration and proportions of the reacting substances, the conditions for obtaining a pure precipitate of magnesium ammonium phosphate are very circumscribed. More concentrated solutions give purer products, and the purity is increased by diminishing as far as possible the quantity of ammonia used. High results are obtained if too little ammonium chloride is used and the solution is not stirred during the precipitation of the magnesium ammonium phosphate.

With regard to the nature of the impurity accompanying the precipitate, the conditions favouring an impure precipitate are those which would be expected to favour the formation of the compounds $Mg[(NH_4)_2PO_4]_2$ and $Mg_3(PO_4)_2$. The former salt, however, should give, on ignition, magnesium metaphosphate, insoluble in hydrochloric acid, but it is found that the precipitate obtained by Schmitz's method is completely soluble, although precipitates formed in the cold contain much metaphosphate (A., 1918, ii, 332). Possibly a second form of metaphosphate exists, soluble in hydrochloric acid, or it may be that other complex compounds are precipitated instead of the above diphosphate. There are grounds for supposing that magnesium ammonium phosphate when ignited undergoes secondary decompositions which have a connexion with the incandescence and blackening which sometimes occur on ignition (compare A., 1917, ii, 90). All experiments on this phenomenon appear to have been made with samples of magnesium ammonium phosphate of doubtful purity, and it is impossible yet to come to any satisfactory conclusions. E. H. R.

Modified Method of Estimating Arsenic as Ammonium Magnesium Arsenate. O. Bailly (*J. Pharm. Chim.*, 1919, [vii], **20**, 55—58).—The ammonium magnesium arsenate precipitate, obtained in the usual way, is washed with dilute ammonia, then

with alcohol to remove free ammonia, and titrated with $N/2$-acid, using methyl-orange as indicator. Each c.c. of $N/2$-acid is equivalent to 0·01875 gram of arsenic. W. P. S.

Iodometric Estimation of Arsenic Acid. I. M. Kolthoff (*Pharm. Weekblad*, 1919, **56**, 1322—1326).—The reaction $As_2O_5 + 4HI \rightleftharpoons As_2O_3 + 2I_2 + 2H_2O$ proceeds from left to right only in strongly acid solution. Accurate titration results are obtained for arsenate concentrations of $N/5$ to $N/10$ with a minimum concentration of hydrochloric acid of $4N$ in the mixture. For more dilute arsenate solutions ($N/50$), a minimum hydrochloric acid concentration of $4{\cdot}5N$ is required. After addition of the iodide and the acid to the arsenate solution, five minutes must elapse before titration with thiosulphate.

Molybdate, tungstate, vanadate, manganous, ferrous, uranyl, and chromic ions appear to have no catalytic effect on the reaction. W. S. M.

Estimation of Free Alkali or Alkali Carbonate Alone or in the Presence of Alkali Hypochlorite. W. Mestrezat (*J. Pharm. Chim.*, 1919, [vii], **20**, 9—14. Compare this vol., ii, 79).—Alkali hypochlorite solution, containing no free alkali hydroxide or carbonate, is neutral towards reagents after the hypochloride has been decomposed by thiosulphate. Free alkali or alkali carbonate in such solution can, therefore, be titrated; alkali carbonates, in the cold and in concentration not exceeding $N/80$, are alkaline towards phenolphthalein, but the alkalinity disappears when the titration has proceeded to the formation of alkali hydrogen carbonate. W. P. S.

Estimation of Free Alkali Hydroxide and Carbonate in Alkali Hypochlorite Solution. Philibert (*J. Pharm. Chim.*, 1919, [vii], **20**, 52—55. Compare this vol., ii, 79).—A reply to Mestrezat (preceding abstract). The author maintains the trustworthiness of the iodo-acidimetric method. W. P. S.

Estimation of Very Small Amounts of Calcium, Magnesium, and Phosphorus in Animal Substances. L. Dienes (*Biochem. Zeitsch.*, 1919, **95**, 131—145).—The methods described are essentially those usually employed, namely, the estimation of calcium as oxalate by titration with permanganate, the estimation of magnesium by the determination of the phosphorus present in the precipitated magnesium ammonium phosphate, and the estimation of phosphorus by titration of the precipitated ammonium phosphomolybdate with standard alkali. The technique of the methods has been suitably modified for the manipulation of very small quantities. J. C. D.

Estimation of Zinc and Calcium in the Presence of Lead. Ernest Nyman (*Chem. News*, 1919, **119**, 75—76).—Zinc and calcium may be estimated in the presence of lead, in such mixtures as are frequently found in pigments, by the following method. An

acid solution of the salts is treated with ammonia until strongly alkaline and then acidified with acetic acid. Should a precipitate be formed it is dissolved by the addition of a few grams of ammonium acetate. When a clear solution is obtained the solution is made slightly alkaline with ammonia and titrated at 70—80° with standard potassium ferrocyanide solution, using an acid solution of uranyl acetate as external indicator. In this way the zinc may be accurately estimated. To estimate the calcium a faintly alkaline solution is prepared as described above, and the calcium precipitated by the addition of an excess of ammonium oxalate. J. F. S.

Alkalimetric Estimation of Small Amounts of Magnesium. P. L. Hibbard (*J. Ind. Eng. Chem.*, 1919, **11**, 753—754).—A method described previously by Bruckmiller (A., 1917, ii, 271) for the titration of ammonium magnesium phosphate is modified by the author in order to render it applicable to the estimation of small amounts of magnesium (5 mg., or less) such as are found in soil extracts. The principal modifications introduced are the use of a Gooch crucible for filtration, whereby the precipitate may be washed with the least possible quantity of solution, washing the precipitate with alcohol and then with a cold saturated ammonium magnesium phosphate solution, and the use of methyl-red as indicator in the titration. W. P. S.

A Colour Reaction which may be Used for the Detection of Mercury in Mercury Compounds. Arthur Abelmann (*Pharm. Zentr.-h.*, 1919, **60**, 247—248).—The following reaction is given by mercury salts and even by organic mercury compounds in which the mercury does not react with hydrogen sulphide. A solution or suspension of the mercury compound is treated with a drop of dilute nitric acid and a moderate quantity of ferrous sulphate solution, and concentrated sulphuric acid is added so as to form a layer under the mixture; a reddish-violet ring is formed at once at the junction of the two liquids. After some time the usual brown ring (nitric acid reaction) appears above the violet ring. W. P. S.

Volumetric Estimation of Mercury Salts and the Estimation of Mercury in Mercury Chloride Compresses. F. Utz (*Pharm. Zentr.-h.*, 1919, **60**, 301—302).—A method described recently by Adanti (A., 1916, ii, 579) was proposed originally by Rupp (A., 1905, ii, 484; 1906, ii, 902), and applied by Utz (A., 1907, ii, 400). W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. L. Brandt (*Chem. Zeit.*, 1919, **43**, 394—397).—The influence of colloidal silica on the titration of ferrous salts with permanganate (compare Schwartz and Rolfes, this vol., ii, 170) in hydrochloric acid solution is not due to its inhibiting action on the reaction between hydrochloric acid and permanganate, since the same effect is noticed in sulphuric acid solutions. The decreased

amount of permanganate required for the titration in the presence of colloidal silica appears to be due to dissolved and atmospheric oxygen, the silica acting as a catalyst in the oxygen–ferrous salt–permanganate reaction. Silica has no influence on the reaction between oxygen and ferrous salts in the absence of permanganate.

W. P. S.

Analysis of Steel. A. Travers (*Ann. Chim.*, 1919, [ix], **11**, 17—128. Compare this vol., ii, 81, 300).—An exhaustive résumé of methods for the estimation of the usual constituents of steels; the original should be consulted for the many methods which are given in detail. [See, further, *J. Soc. Chem. Ind.*, 724A.]

W. P. S.

Estimation of Iron, Zinc, Copper, and Aluminium in Aluminium Alloys. Paul Holmsen (*Tidskr. Kemi. Farm. Ter.*, 1919, **16**, 62—63).—The separation of copper, iron, aluminium, and zinc is effected by treating the sample with 30% sodium hydroxide solution, using 50 c.c. for a 3-gram sample. When the aluminium and zinc are in solution, water is added, and the residue of iron and copper removed by filtration. Aluminium is separated from zinc and iron from copper by adding ammonia to the acid solutions of these two pairs, and the four metals are estimated by well-known methods.

Chemical Abstracts.

Electrolytic Estimation of Nickel and Cobalt. Motooki Matsui and Tadasu Nakazawa (*J. Tokyo Chem. Soc.*, 1919, **40**, 339—349).—Nickel and cobalt can be precipitated quantitatively from their dimethylglyoxime salts by electrolysis. The following modification is therefore substituted for the usual method. To the mixture of nickel and cobalt, sodium acetate and an excess of dimethylglyoxime (0·2 gram) are added until the precipitation of nickel is complete. The precipitate is washed, dissolved in sodium hydroxide (4·8 grams), and estimated by electrolysis. To the filtrate is added sodium hydroxide, and the cobalt estimated similarly. When the amount of nickel exceeds 0·058 gram in 100 c.c., an addition at the positive pole of a few drops of a mixture containing 5 c.c. of glycerol, 45 c.c. of alcohol, and 50 c.c. of water is necessary in order to prevent deposition of the oxide at the pole. When cobalt is present in a high concentration, the similar oxide deposit can be prevented if aqueous ammonia (50 c.c.) containing 2 grams of ammonium sulphate, to increase the conductivity, is substituted for sodium hydroxide. From a mixture containing 0·0102 gram of nickel and 0·1836 gram of cobalt made up to 100 c.c., using 3·2 volts for nickel, 3·8 volts for cobalt, with one ampere current, were obtained 0·0100 gram of nickel after 2·5 hours and 0·1834 gram of cobalt after 3·3 hours at the ordinary temperature. The temperature should always be kept under 50°, otherwise the positive pole will be coated with the oxide.

Chemical Abstracts.

Analysis of Alloys of Tin. Archibald Craig (*J. Ind. Eng. Chem.*, 1919, **11**, 750—753).—A discussion of the conditions giving the most trustworthy results in the analysis of tin alloys by the nitric acid separation method; the processes for the various separations and purification of the precipitates, etc., are given in detail. W. P. S.

Separation of Tin, Antimony, and Arsenic by Plato's Method. Willy Hartmann (*Zeitsch. anal. Chem.*, 1919, **58**, 148—156).—Modifications of this method (A., 1910, ii, 903) are described. After antimony and arsenic have been distilled, as in the original method, the residue is treated with a mixture of hydrobromic and hydrochloric acids, and the tin distilled at 130° to 140° in a current of carbon dioxide. Arsenic is separated by treating the distillate, in the cold, with hydrogen sulphide; the arsenic trisulphide is collected on a filter, and the antimony is also precipitated as sulphide after the filtrate has been neutralised with ammonia. W. P. S.

Estimation of Cerium in the Presence of other Rare Earths by Precipitation as Ceric Iodate. Paul H. M.-P. Brinton and C. James (*J. Amer. Chem. Soc.*, 1919, **41**, 1080—1085).—Solutions containing rare earth nitrates (thorium having been removed) may be quantitatively analysed for cerium as follows: the solution is treated with half its volume of nitric acid; the whole solution at this stage should not be more than 75 c.c., and the amount of cerium oxide should not exceed 0·15 gram; 0·5 gram of potassium bromate is added, and when it has dissolved ten to fifteen times the theoretical quantity of potassium iodate is added in nitric acid solution (100 grams iodate, 333 grams acid) with constant stirring. The ceric iodate is allowed to settle and filtered on a paper of close texture. After draining, the precipitate is washed back into the beaker by means of a solution containing 8 grams of potassium iodate and 50 c.c. of nitric acid per litre. The precipitate is well mixed with the washing solution and brought back on to the same filter paper. It is then rinsed back into the beaker with hot water, heated to boiling, and treated drop by drop with nitric acid until it is entirely dissolved. To this solution, 0·25 gram of potassium bromate and as much iodate as was previously used are added. The precipitate is allowed to settle and then filtered through the same filter paper, and washed once with the washing solution. It is brought back into the beaker, well stirred, and again filtered and washed with three small portions of the washing solution. The filter paper and precipitate are now dropped into the original beaker, and 5—8 grams of oxalic acid and 50 c.c. of water are added. The beaker is covered and gently heated, and then boiled until iodine is no longer expelled. The precipitate is kept several hours,

filtered, washed, dried, and ignited to oxide, which is weighed. This method is trustworthy even in the presence of large quantities of the other rare earths. J. F. S.

Electrometric Titration of Vanadium. Selective Oxidation of Vanadyl Salts in Presence of Chromic Salts. G. L. KELLEY, J. A. WILEY, R. T. BOHN, and W. C. WRIGHT (*J. Ind. Eng. Chem.*, 1919, **11**, 632—634).—For the estimation of small quantities of vanadium in steel by the method of electrometric titration (A., 1917, ii, 512), the sample is dissolved in sulphuric acid and the vanadium oxidised by boiling with nitric acid under specified conditions. This oxidises vanadyl compounds to the extent of about 99% without oxidising chromic compounds. The liquid is then cooled and titrated by the electrometric method with ferrous ammonium sulphate which has been standardised against potassium dichromate solution. A correction is subsequently made for the 1% of unoxidised vanadium. In estimating chromium in chrome–vanadium steels, the solution, obtained as described, is oxidised with nitric acid, and then treated with silver nitrate solution and ammonium persulphate solution, boiled to decompose the excess of persulphate, acidified with hydrochloric acid, boiled and cooled, and the chromium and vanadium titrated together. The vanadium end-point is that previously described (*loc. cit.*). The result for vanadium is expressed in its equivalent of chromium and deducted from the total dichromate solution used in the titration of the chromium and vanadium. [See also *J. Soc. Chem. Ind.*, 1919, 583A.] C. A. M.

Microchemical Reaction of Various Bismuth Compounds. G. DENIGÈS (*Bull. Soc. pharm. Bordeaux*, 1919; from *Ann. Chim. anal.*, 1919, [ii], **1**, 213—214).—A drop of dilute hydrochloric acid and a drop of 5% hexamethylenetetramine solution are mixed on a microscope slide, and a drop of a bismuth solution or a small particle of an insoluble bismuth compound is brought into contact with the mixture. On examining the preparation under the microscope (a cover-glass is not used), characteristic crystals are observed, mainly at the point of contact. The crystals are colourless and have the form of hexahedra, hexagonal plates, dodecahedra, or rhombic octahedra. The crystals may be obtained from practically all bismuth compounds. W. P. S.

Electroanalysis of Bismuth and its Ores. MANZO NAKAO (*J. Pharm. Soc. Japan*, 1919, No. 446, 275—307).—The formation of spongy and loose granular precipitates at the negative pole is one of the sources of error and difficulties in the electroanalysis of bismuth. Sand's method, although it prevents the formation of the spongy deposit, does not produce sufficiently permanent precipitates that will not easily peel off on drying. The

author modifies the methods used by Sand and Fischer by proposing the use of a very small amount of colloidal substances. An addition of 1 mg. of gum arabic to 100 c.c. of the solution not only produces a more permanent precipitate of bismuth, but also gives a quantitative yield in ten minutes. In separating bismuth from copper, the formaldehyde used by Sand to prevent the formation of bismuth oxide is replaced by borax and hydroxylamine sulphate. The best result is obtained by using sodium tartrate 4 grams, sodium hydroxide 4 grams, potassium cyanate 3·5 grams, hydroxylamine 0·5—1 gram, borax 2—1 grams, made up to 120 c.c., stirring at the rate of 1200 revolutions per minute at 65° for twenty minutes, employing 0·4—0·2 ampere, and maintaining 1·2—1·7 volts at the poles. Under this condition, 0·3131 gram out of 0·3130 of bismuth is obtained in the separation from 0·3 gram of copper. In estimating bismuth in bismuth ores, after removing tin and lead, instead of using hydrogen sulphide, ammonia and ammonium chloride are employed, the mass is dissolved in as little nitric acid as possible, and 4 grams of tartrate, 2 grams of sodium hydroxide, 5 grams of potassium cyanate, and 1 gram of hydroxylamine are added, the volume being made up to 120 c.c., and a current of 1·2 volts used. When the voltage exceeds 1·2, the current is changed to 0·1 ampere; above 1·8 volts, 2 amperes, and finally 0·5 ampere, of current are used for thirty-five minutes (70—80°), stirring at the rate of 1000 revolutions per minute.

CHEMICAL ABSTRACTS.

Estimation of the Inorganic Constituents of Blood and other Physiological Material. ISIDOR GREENWALD (*J. Biol. Chem.*, 1919, **38**, 439—440).—Proteins and fats are removed from the blood by precipitation with picric acid. The oxidation of the filtrate for the purpose of estimating the inorganic constituents is then an easy matter. J. C. D.

Use of the Critical Temperature of Solution in Aniline in the Summary Analysis of a Petroleum. G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **169**, 70—73).—By summary analysis, the authors mean a determination of the percentage of aromatic hydrocarbons (Ar), saturated cyclic hydrocarbons (C), and acyclic hydrocarbons (Ac) present in the petroleum. The critical temperatures of solution of the petroleum in aniline are determined before and after its treatment with a mixture of sulphuric and nitric acids to remove the aromatic hydrocarbons, the two values obtained being respectively T_1 and T_2. Then the respective percentages may be calculated from the three formulæ $Ar = 1{\cdot}18(T_2 - T_1)$, $C = [72 - (T_2 + 0{\cdot}2)](100 - Ar)/(72 - 39{\cdot}5)$, and $Ac = 100 - Ar - C$. These formulæ contain all necessary corrections except for the presence of ethylenic hydrocarbons. If these are present, for T_1 must be written $T_1 + 0{\cdot}4E$, where E is the percentage of ethylenic hydrocarbons expressed as amylene. W. G.

Critical Temperatures of Solution in Aniline of Mixtures of Hydrocarbons. Application to the Analysis of Petroleum. G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **169**, 185—188. Compare preceding abstract).—A mixture of two acyclic hydrocarbons or a mixture of one acyclic and one saturated cyclic hydrocarbon obeys the law of additivity in so far as its critical temperature of solution in aniline is concerned, but a mixture of two saturated cyclic hydrocarbons does not obey this law. If to a mixture of hydrocarbons, devoid of aromatic hydrocarbons, benzene is added to an extent not exceeding 10—15%, then the depression of the critical temperature of solution in aniline is proportional to the percentage of benzene added, the ratio being 1:1·14. Similarly, for toluene the ratio is 1:1·19 and for xylene 1:1·24. The above results furnish the basis for the method of analysis of petroleum previously outlined (preceding abstract), it being necessary first to fractionate the petroleum so that there is only one saturated cyclic hydrocarbon in each fraction. W. G.

The Composition of some Asiatic Petroleums. G. CHAVANNE and L. J. SIMON (*Compt. rend.*, 1919, **169**, 285—288).—Using the analytical method based on the critical temperature of solution in aniline, previously described (this vol., ii, 267; preceding abstracts), the authors have determined the composition of petroleums coming from Persia, Sumatra, and Borneo. The Persian and Sumatran petroleums are particularly rich in acyclic hydrocarbons. The Borneo petroleum was fractionated, and the different fractions were examined separately. Further details are given for the correction necessary in the calculation due to the presence of ethylenic hydrocarbons. W. G.

Estimation of Thiophen. PERCY E. SPIELMANN and S. P. SCHOTZ (*J. Soc. Chem. Ind.*, 1919, **38**, 188—189T).—A modified basic mercuric sulphate method is recommended for the estimation of thiophen in benzene. Two c.c. of the sample are shaken for three hours in a closed tube with 20 c.c. of basic mercuric sulphate solution (sulphuric acid, 20 c.c.; mercuric oxide, 5 grams; water, 100 c.c.). The precipitate formed is collected, washed with hot water, dried at 110°, and weighed; its weight multiplied by 0·0757 gives the amount of thiophen in 2 c.c. of benzene. Another, but less convenient, method consists in heating 10 c.c. of the benzene at 100° for fifteen minutes with 4 grams of basic mercuric acetate (glacial acetic acid, two parts; mercuric oxide, one part). After cooling, the precipitate is collected, washed with water, dried at 100°, and weighed. In this case, the factor is 0·07516. W. P. S.

Use of Refraction in Analysis. O. FAUST (*Zeitsch. anal. Chem.*, 1919, **58**, 145—148).—The refractometer may be used for estimating alcohol in mixtures of alcohol and water, provided that the amount of alcohol lies between 0 and 40%. The maximum refraction is given by alcohol of about 80%, and decreases as the

concentration rises or falls, so that between 50 and 100% there are always two mixtures having the same refraction. W. P. S.

Estimation of Ethyl Alcohol in the Presence of Volatile Substances, especially Aldehyde and Acetone, and the Simultaneous Estimation of the Latter. KARL HOEPNER (*Zeitsch. Nahr. Genussm.*, 1917, **34**, 453—466).—The following procedure is recommended for the estimation of ethyl alcohol, acetaldehyde, and acetone in a mixture of the same in aqueous solution. Ethyl alcohol and acetaldehyde are oxidised to acetic acid by means of chromic acid and sulphuric acid; the unchanged acetone is then distilled and converted into the ketoxime by treatment with hydroxylamine hydrochloride; an equivalent quantity of hydrochloric acid is liberated in the reaction, and its titration gives the amount of acetone present. Acetaldehyde and acetone are then converted into the aldoxime and ketoxime by similarly treating a quantity of the original solution with hydroxylamine hydrochloride: the difference between the quantity of hydrochloric acid liberated in this and in the previous experiment is a measure of the aldehyde present. Ethyl alcohol and acetaldehyde are then estimated together by oxidation with chromic acid. [See, further, *J. Soc. Chem. Ind.*, 1919, 735A.] W. P. S.

Titration of Sugars. E. RUPP and F. LEHMANN (*Zeitsch. Nahr. Genussm.*, 1919, **37**, 162—164).—Further experience confirms the trustworthiness of the method described previously by the authors (A., 1909, ii, 442). If desired, the sugar solution may be mixed with the cold Fehling's solution and water, and the mixture then boiled, etc., as described. (Compare also Frerichs and Mannheim, A., 1917, ii, 393.) W. P. S.

Influence of Acetone on Bang's Method of 1914 for the Estimation of Sugar. N. O. ENGFELDT (*Svensk Farm. Tidskr.* 1919, **23**, 301—308).—The statement has been made by G. Engstrand that acetone reacts with the iodine in the Bang method for the estimation of sugar in blood and urine, causing an error in the results. The author has made several careful tests, using blood, acetone, and β-hydroxybutyric acid. The titrations were not affected by these two substances, and the results in using this method are trustworthy. CHEMICAL ABSTRACTS.

Estimation of Sugar in Blood. HUGH MACLEAN (*Biochem. J.*, 1919, **13**, 135—147).—Improvements and simplification of the method previously published by the author (A., 1916, i, 613) are described. The greater part of the protein is removed by heating with an acetic acid–sodium sulphate solution, the remainder being removed by a small quantity of dialysed iron. The sugar in an aliquot portion of the protein-free filtrate is estimated by boiling with an alkaline copper solution containing potassium iodide and iodate. Careful regulation of the boiling is necessary to ensure accurate results. The solution containing the cuprous oxide in

suspension is cooled, treated with a slight excess of hydrochloric acid, and the free iodine titrated with sodium thiosulphate. The method yields accurate results with as little as 0·2 c.c. of blood.

J. C. D.

The Picric Acid Method for the Estimation of Sugar in Blood, and a Comparison of this Method with that of Maclean. Owen Lambert Vaughan de Wesselow (*Biochem. J.*, 1919, **13**, 148—152).—A study of the two methods indicated that the results yielded by Benedict's method were invariably higher than those obtained by Maclean's method (see preceding abstract). The possible causes of the discrepancy were considered, and it was found that the high figures given by the first-named method appear to be chiefly due to the presence of an interfering substance or substances, mainly concentrated in the corpuscles, which reacts with the picric acid solution at an early stage of the heating. The Maclean method is therefore considered to be the more accurate one of the two. J. C. D.

Lewis-Benedict Method of Estimating Blood Sugar. Sergius Morgulis and H. M. Jahr (*J. Biol. Chem.*, 1919, **39**, 119—123).—The presence of creatinine increases the blood sugar value as determined by the Lewis-Benedict method, particularly in the analysis of pathological bloods when the blood creatinine may be high (compare de Wesselow, preceding abstract). J. C. D.

The Cuprous Chloride-Iodine Method for Reducing Sugars Simplified. F. M. Scales (*J. Ind. Eng. Chem.*, 1919, 11, 747—750. Compare A., 1916, ii, 117; 1917, ii, 276).—Twenty c.c. of modified Benedict's solution (copper sulphate, 16·0 grams; sodium citrate, 150 grams; anhydrous sodium carbonate, 130 grams; sodium hydrogen carbonate, 10 grams per litre) and 10 c.c. of the sugar solution (containing not more than 0·02 gram of dextrose) are mixed, heated gradually so as to boil in five minutes, boiled for a further three minutes, and cooled rapidly. The solution is acidified with 100 c.c. of dilute acetic acid, an excess of iodine solution is added, followed by 25 c.c. of dilute hydrochloric acid, and the excess of iodine is titrated with thiosulphate solution after the lapse of one minute. The thiosulphate solution may be standardised against known amounts of dextrose; the ratio of reducing sugar to thiosulphate is constant. W. P. S.

Studies in Steam Distillation. The Possibilities and Limitations of Duclaux's Method for the Estimation of Homologous Acids. H. Droop Richmond (*Analyst*, 1919, **44**, 255—274. Compare A., 1917, i, 316).—A series of tables is given recording the author's experimental results and showing the quantity of each acid distilled for each 10% by volume distilled, the tables being divided according to the initial strength of acid. Methods of calculation are discussed, and the application of

Duclaux's method in analysis is described; attention is drawn to its usefulness in estimating volatile acids, the purity of an acid, the quantity of impurity present, etc. W. P. S.

Estimation of β-Hydroxybutyric Acid, Acetoacetic Acid, and Acetone in Blood. Donald D. van Slyke and Reginald Fitz (*J. Biol. Chem.*, 1919, **39**, 23).—In the process previously described by these authors (A., 1918, ii, 86) it is necessary that the precipitate should be filtered soon after the period of boiling is ended. J. C. D.

Detection of Formaldehyde and Hexamethylenetetramine in Urine. F. Utz (*Süddeut. Apoth. Zeit.*, 59, 55—56, 64; from *Chem. Zentr.*, 1919, ii, 820—821).—The author's investigations show that the time within which formaldehyde can be detected in the urine after administration of hexamethylenetetramine varies in an extraordinary degree; generally an hour elapses before the detection is successful. The most suitable methods are those of Lebbin, Salkowski, Jorrisen and Judd, Collins and Hanzlik, and, particularly, the phenylhydrazine test described by Arnold and Mentzel. When the amount of formaldehyde is very small or the urine is deeply coloured, the specimen is conveniently treated with phenylhydrazine and potassium ferricyanide and shaken with ether; the ethereal solution is agitated with concentrated hydrochloric acid. The red coloration thereby produced appears in the acid layer after the two liquids have separated.

The main portion of hexamethylenetetramine separates as such in the urine. Mercuric chloride in the presence of 10% of alcohol is a suitable precipitant for hexamethylenetetramine, the mode of operation recommended by Schröter being particularly suitable. Precipitation by bromine water gives a useful qualitative test for the presence of hexamethylenetetramine in urine. Esbach's method cannot be applied to the estimation of albumin in urines which contain hexamethylenetetramine; care is also necessary in testing such urines for sugar. H. W.

Titration of *p*-Aminoazobenzene. F. Neitzel (*Chem. Zeit.*, 1919, **43**, 472).—Trustworthy results may be obtained by diazotising the substance in acid-alcoholic solution. One gram of the sample is dissolved in 100 c.c. of alcohol and 5 c.c. of hydrochloric acid, D 1·19, and the solution is titrated with standardised nitrite solution; iodide–starch paper is used as an external indicator. W. P. S.

Applicability of Cuprammonium Sulphate for the Acidimetric Estimation of Alkaloids according to E. Falières. Hermann Kunz-Krause and Rudolf Richter (*Arch. Pharm.*, 1917, **255**, 507—513).—The method suggested by Falières (A., 1899, ii, 713) for the acidimetric estimation of alkaloids in their pure solutions by means of standard cuprammonium solution yields satisfactory results, although the high value of the ratio between corresponding volumes of *N*/10-sulphuric acid and the cuprammon-

ium solution detracts from its sensitiveness; the latter is indeed far below the sensitiveness of the iodeosin method, which admits of the use of $N/100$-solutions. The Falières method cannot be applied to the estimation of alkaloids in tinctures, extracts, etc., preliminary separation of the alkaloids being necessary if it is to be employed. [See *J. Soc. Chem. Ind.*, 1919, 737A.] T. H. P.

Estimation of Caffeine in Vegetable Material. FREDERICK B. POWER and VICTOR K. CHESNUT (*J. Amer. Chem. Soc.*, 1919, **41**, 1298—1306).—The process for estimating caffeine in tea, described in Allen's "Commercial Organic Analysis," has been considerably modified so as to make it suitable for the analysis of vegetable material generally. The new method is as follows. Ten grams of the finely ground material are extracted for about eight hours with hot alcohol, the extract is added to a suspension of 10 grams of heavy magnesium oxide in 100 c.c. of water, and the whole slowly evaporated nearly to dryness, with frequent stirring. The powder is transferred to a smooth filter and washed with hot water until about 250 c.c. of filtrate collects, when the solution is mixed with 10—20 c.c. of 10% sulphuric acid, and then boiled in a litre flask for about thirty minutes, in order to hydrolyse saponins. The cooled liquid is filtered through a moistened paper into a separating funnel, and shaken with six portions of chloroform of 25 c.c. each. The extracts are decolorised by shaking with 5 c.c. of 1% potassium hydroxide, then run through a dry filter into a conical flask and evaporated, and the caffeine is transferred to a tared beaker and dried in a water-oven. Generally speaking, the residue is nearly white.

Some examples of the application of the method to teas, coffee, coffee leaves and pulp, and guarana are recorded. It is also stated that the "Forest tea" of the Philippines, *Ehretia macrophylla*, Wall, the "New Jersey tea," *Ceanothus Americanus*, Linn., and the "wild coffee" of Florida, *Psychotria undata*, Jacq., do not contain caffeine. J. C. W.

Estimation of Morphine and Solubility of Morphine in Ammonia. A. HEIDUSCHKA and M. FAUL (*Arch. Pharm.*, 1917, **255**, 441—466).—The solubility of morphine in ammonia solutions is found to be proportional to the concentration of the hydroxyl ions of the solution. From the solubility results, a formula is elaborated for correcting the values given by the method of estimating morphine in opium based on the precipitation of the base by ammonia. [See *J. Soc. Chem. Ind.*, 1919, 737A.] T. H. P.

Estimation of Quinine in Urine. BAUR and REVEILLET (*Union pharm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], **1**, 214—215).—Five c.c. of the filtered urine containing quinine are mixed with 5 c.c. of picric acid solution, and the turbidity obtained is compared with that produced by known amounts of quinine added to normal urine and treated similarly. The method cannot

be applied to urines containing albumin, large quantities of potassium or ammonium salts, or urates. W. P. S.

Specific Colour Reaction of Oxalates. H. Caron and D. Raquet (*Ann. Chim. anal.*, 1919, [ii], **1**, 205).—A reaction described previously (this vol., ii, 351) for the detection of manganese may be used inversely for the detection of oxalates. A red coloration is obtained when an oxalate solution is treated with two drops of 10% manganese sulphate solution, 1 c.c. of acetic acid, and one drop of potassium dichromate solution or a few drops of alkali hypochlorite solution. In the case of an acid solution or of oxalic acid itself, the acetic acid used in the test should be replaced by sodium acetate. The coloration may be obtained with 0·1 gram of oxalic acid; phosphoric acid and hydrofluoric acid do not interfere with the test. W. P. S.

Glucosides with Digitalis-like Action. A New Characteristic Reaction. H. Baljet (*Pharm. Weekblad*, 1918, **55**, 457—467).—Digitalin gives a deep red coloration with picric acid and potassium or sodium hydroxide. Gitalin, digitoxin, anhydrogitalin, strophanthin, and *K*-strophanthin give an orange-red coloration with the same reagents. All these glucosides exert an action similar to that of digitalis on the heart. Digitonin, arbutin, amygdalin, and condurangin do not respond to the test. The author suggests that the effect is due to the presence of the carbonyl group linked directly to a carbon atom, such as occurs in the lactone structure of the digitalis glucosides. A positive reaction is also obtained with peptones, probably owing to the presence of creatinine, with acetone, and with aldoses. W. S. M.

A Revised Colorimetric Method for the Estimation of Uric Acid in Urine. Otto Folin and Hsien Wu (*J. Biol. Chem.*, 1919, **38**, 459—460).—The method previously described for the estimation of uric acid in blood (Folin and Wu, this vol., ii, 308) may be employed in the analysis of urine. J. C. D.

A Colour Reaction of the Proteins. S. Edlbacher (*Zeitsch. physiol. Chem.*, 1919, **105**, 240—241).—The protein solution is shaken with a solution of sodium hydroxide and methyl sulphate, and, after the decomposition of the latter, concentrated sulphuric acid is added so as to form a layer at the bottom. At the surface of contact of the two layers a reddish-blue colour develops, and, on shaking, the whole liquid assumes this colour.

The coloration resembles that produced in the glyoxylic acid reaction, and, as in that test, is produced by tryptophan. Indole and scatole give a red coloration. The test is regarded as more sensitive than the bromine reaction for free tryptophan.

J. C. D.

The Starch-Iodine Reaction and its Application in the Colorimetric Estimation of Proteins in Immunity Reactions. C. Lange (*Biochem. Zeitsch.*, 1919, **95**, 46—84).—A very full discussion of the reaction of starch with iodine, including a

criticism of Wohlgemuth's method for estimating diastase. The reaction between starch and iodine may be influenced by the presence of other substances, particularly protein, and this fact is made the basis of a method for estimating protein in such fluids as blood, plasma, serum, or bacterial vaccines. The fluids to be compared are treated with a solution of iodine, and, after suitable dilution, are heated for half an hour on the water-bath at 40°. Starch is then added and the colours compared. This process may be used for the standardisation of vaccines. J. C. D.

Application of Pyramidone in Analysis. Escaïch (*J. Pharm. Chim.*, 1919, [vii], **20**, 49—52).—Pyramidone in acid solution gives a blue coloration with many oxidising substances (nitrites, ferric chloride, hydrogen peroxide, etc.), but if pyridine is added, a sensitive reagent is obtained for the detection of anæroxydases in blood, raw milk, etc. A blue coloration develops when 1 c.c. of urine containing blood is added to a mixture of 1 c.c. of pyridine, 1 c.c. of pyramidone solution, two drops of hydrogen peroxide, and a few drops of acetic acid. A mixture of pyramidone, dilute copper sulphate solution, and acetic acid gives a blue coloration and a turbidity when treated with a few drops of hydrocyanic acid solution; inversely, this reaction may be used for the detection of copper. W. P. S.

Methods of Blood Analysis. I. Critical Review of the Methods for Removing Proteins. M. Richter-Quittner (*Biochem. Zeitsch.*, 1919, **95**, 179—204).—The importance of this phase of blood analysis is emphasised. Removal of proteins by means of precipitation with salts of heavy metals results in low values being obtained for non-protein nitrogen in the filtrate, because the precipitate adsorbs substances such as urea and creatinine. The same drawback applies to the use of colloidal precipitants such as dialysed iron. The removal of proteins by heat is very difficult to carry out satisfactorily.

Of the acid precipitants, the author gives the preference to trichloroacetic acid, but, as in the case of heat precipitation, the values for non-protein nitrogen tend to be high.

A modification of Folin's method for removing protein by methyl alcohol and zinc chlorides is described which gives trustworthy results. J. C. D.

Precipitation of Proteins by Ammonium Sulphate and Biochemical Reactions. A. Ch. Hollande (*Compt. rend. Soc. Biol.*, 1919, 567; from *J. Pharm. Chim.*, 1919, [vii], **20**, 92—94).—Preliminary precipitation of proteins by ammonium sulphate is recommended before precipitin reactions are applied. For instance, urine containing ovalbumin is saturated with ammonium sulphate, the precipitate collected, washed with saturated ammonium sulphate solution, then dissolved in sodium chloride solution, and the albumin identified by precipitin reactions.

W. P. S.

Identification of Pharmaceutical Disulphones, Sulphonal, Trional, and Tetronal. J. A. Sanchez (*El Restaurador farm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], **1**, 228—229).—The three substances yield iodoform when treated as follows: A mixture of equal quantities of the sulphone and manganese dioxide is heated in a test-tube, and the vapours evolved are collected in a small quantity of water contained in a second test-tube; the solution thus obtained has an odour of ethyl mercaptan, and when rendered alkaline with sodium hydroxide, heated, and treated with iodine solution, yields iodoform. The three substances may be distinguished from one another by the melting points and by their different solubilities in ether. One gram of sulphonal dissolves in 133 c.c. of ether, 1 gram of trional in 15·57 c.c., and 1 gram of tetronal in 9·83 c.c. W. P. S.

Identification and Assay of Pharmaceutical Disulphones. Schamelhout (*J. Pharm. Belg.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], **1**, 259—260).—Several errors in a recent paper by Sanchez (preceding abstract) are pointed out; sulphonal, trional, and tetronal do not contain a CO group, the ethylsulphonic group does not contain a CH_3 group, and the iodoform reaction is not characteristic of ethylsulphonic groups. W. P. S.

Silver Sodium Salvarsan. I. A. Binz (*Arbb. aus. Inst. exp. Therapie Georg. Speyer Hause*, 1919, **7**, 43—47; from *Chem. Zentr.*, 1919, iv, 37).—Silver is deposited as silver oxide when silver sodium salvarsan is oxidised by hydrogen peroxide in alkaline solution, and the arsenic is converted into a state in which it can readily be detached from the nucleus in the form of arsenic acid, the latter process being advantageously effected with sodium hypochlorite. The method of removing arsenic from organic compounds is not universally applicable in its present form; arsenobenzene gave low results. The analysis of silver sodium salvarsan is performed as follows: The substance (0·6232 gram) is heated to boiling for an hour with water (30 c.c.) and perhydrol (6 c.c.); after addition of concentrated nitric acid (9 c.c.), the solution is evaporated to dryness, when the silver (except for a trace of silver chloride due to the presence of sodium chloride in the preparation) is converted into silver nitrate. The residue is boiled under a reflux condenser for an hour with a solution of sodium hypochlorite (30 c.c.), whereby the silver is completely converted into silver chloride and the arsenic is eliminated. [The hypochlorite solution is prepared by dropping a mixture of water (11 c.c.) and hydrochloric acid (D 1·19; 84 c.c.) on potassium permanganate (13 grams), and absorption of the chlorine in sodium hydroxide solution (10*N*; 60 c.c.) and water (150 c.c.)]. Arsenic is estimated in the filtrate by means of magnesia mixture after decomposition of the excess of hypochlorite with boiling hydrochloric acid, dilution with water, and filtration of silver chloride. H. W.

General and Physical Chemistry.

Measurements in the Arc Spectrum of Iron for the Purpose of Determining Tertiary Normals. Sophie Hoeltzenbein (*Zeitsch. wiss. Photochem.*, 1917, **16**, 225—251).—Making use of a concave grating, 4 metres radius and 3960 lines per centimetre, the author has re-measured the iron arc spectrum over the range λλ 5658—4859 in the third order spectrum, λλ 4315—3513 in the fourth order spectrum, and λλ 3513—2987 in the fifth order spectrum. Long tables of the wave-length and intensity of the measured lines are given, and an accuracy of about 0·001 Å. is claimed for the values of the wave-lengths. A comparison of the present results with those of Gale and Adams (*Astrophys. J.*, 1912, 35) and St. John and Ware (*ibid.*, 1912, **36**, 14, 203) has been made, and it is shown that very many lines may be used as tertiary normals, and further, that among the lines chosen as tertiary normals very great divergencies are to be observed in the values of the different observers, and consequently more work is necessary before the tertiary normals can be finally chosen. J. F. S.

Series System in the Spectrum of Gold. W. M. Hicks (*Phil. Mag.*, 1919, [vi], **38**, 1—31).—A theoretical discussion of the series systems of the gold spectrum. It is shown that a D set corresponding with order $m=1$ exists, which extends far in the ultra-red, and the satellite mantissa of which conforms to the general rule of being a multiple of Δ. Gold, therefore, does not constitute an exception, as formerly appeared to be the case. It is indicated that summation lines for the P and S series exist. In general, such lines for S and P will lie far down in the ultra-violet, and this is, no doubt, one reason why they have not been previously recognised. The evidence given in the paper must be supported by further numerical coincidences obtained in other spectra before it is to be regarded as conclusive, but it is sufficient to render it extremely probable. The more accurate determination of the oun depending on $81\delta=\Delta=113951-6p$, where $0{\cdot}1p$ Ångström is an observational error, has been carried out. This result gives $\delta=1406{\cdot}802-0{\cdot}074p$. Taking the ratio of $\delta : (W/100)^3$, where W is the atomic weight, to be $361{\cdot}75+0{\cdot}05q$, the resulting value of the atomic weight of gold is $197{\cdot}2024-0{\cdot}0052p-0{\cdot}0136q$. J. F. S.

The Constitution of the Atom and the Properties of Band Spectra. H. Deslandres (*Compt. rend.*, 1919, **169**, 593—599. Compare this vol., ii, 310).—A mathematical discussion in which the author shows that band spectra may be considered as formed by longitudinal and transverse vibrations, the exact part which each plays not being, as yet, fully determined. Two formulæ are deduced which account for the known facts, their

interpretation admitting of longitudinal and transverse vibrations in the atom and molecule, analogous to those in solids. W. G.

The Conditions of Excitation of Fluorescence. L. Bruninghaus (*Compt. rend.*, 1919, **169**, 531—534).—The phenomena of phosphorescence and fluorescence are characterised by the fact that the maximum effect is obtained when the solution is very dilute and the exciting radiation only very feebly absorbed. W. G.

Photochemical Change in the System $SO_2Cl_2 \rightleftharpoons SO_2 + Cl_2$ under the Influence of Light Rays of Definite Wave-length. M. Le Blanc, K. Andrich, and W. Kangro (*Zeitsch. Elektrochem.*, 1919, **25**, 229—251).—A long series of experiments are described which are designed to furnish answers to the questions arising from the following case. Given an homogeneous gaseous system, $A + B \rightleftharpoons C$, which is sensitive to light and such that the absorption spectra of A, B, and C respectively do not overlap one another, and which has a zero velocity when in the dark, does the whole system become sensitive to light if it is subjected to light which is absorbed by only one constituent, and, if so, to what extent does the reaction proceed in the direction of C? The case $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$ has been examined with the object of answering the questions. The absorption spectra of sulphur dioxide, chlorine, and sulphuryl chloride have been determined at a series of pressures, and it is shown that chlorine absorbs all light from the visible region to the middle ultra-violet, and has a maximum at 340 $\mu\mu$; sulphur dioxide has an absorption maximum at 290 $\mu\mu$ and a minimum at 240 $\mu\mu$; sulphuryl chloride vapour absorbs light from 300 $\mu\mu$ upwards. Experiments on the decomposition of sulphuryl chloride by light at a series of temperatures, the formation of gaseous sulphuryl chloride, and the formation of liquid sulphuryl chloride are described. It is shown that in the reaction $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$ the formation of secondary products does not occur to the extent of 10%. The illumination of sulphuryl chloride by light, which is practically only absorbed by this substance, brings about quantitative decomposition at both 55° and 100°. The concentration has apparently no influence on the course of the reaction. When the system $SO_2 + Cl_2$ is illuminated with light which is absorbed by sulphur dioxide, only a slight reduction of pressure takes place; this is not due to the formation of sulphuryl chloride, but to a side reaction. When the same system is illuminated by light which is only absorbed by chlorine, the formation of sulphuryl chloride takes place until, after a time, a stationary condition is set up. The velocity and also the position of the stationary condition depend, at constant temperature, on the presence of a small quantity of water, and the higher the temperature the earlier the stationary condition is reached. In a number of cases a reversal is noted, so that the stationary condition does not come at the end of diminution of pressure, but of an increase in pressure. At the temperatures 105° and 125°, at which the equili-

brium in the dark is known, the stationary condition lies more to the side of sulphuryl chloride than in the non-illuminated reaction. Under none of the experimental conditions do the two points coincide. The lower the temperature the further apart are the end-points of the illuminated and the non-illuminated reactions. The temperature-coefficient of the formation of sulphuryl chloride from chlorine and sulphur dioxide by light which is only absorbed by chlorine is small, and has little influence on the course of the reaction. J. F. S.

Photochemical Reactions of Compounds of Less Common Elements. II. Alfred Benrath (*Zeitsch. wiss. Photochem.*, 1917, **16**, 253—261. Compare A., 1915, ii, 504).—An aqueous solution of ammonium molybdate when diluted with an equal volume of either ethyl alcohol or methyl alcohol and exposed to sunlight changes to blue after a short exposure and a reddish-brown substance is deposited on the side of the flask on which the light falls. This compound has the formula $(NH_4)_2MoO_4,2MoO_3,2MoO_2,6H_2O$. In this formation only the complex added group, MoO_3, and not the neutral ammonium molybdate is reduced. Colloidal molybdic acid is rapidly reduced by alcohol to the blue oxide, Mo_3O_8. Neutral sodium tungstate is only slowly reduced by alcohol in sunlight, so that after a period of five months' exposure to light only a faint blue colour is produced. On the other hand, suspensions of tungstic acid and acidified solutions of tungstates become deep blue in colour when mixed with alcohol and exposed to sunlight for a few hours. The greenish-yellow powder deposited when uranyl chloride dissolved in ether is exposed to sunlight has been examined and found to have the formula $UOCl_2$, and the similar precipitate obtained by exposing an aqueous solution of uranyl nitrate containing a little alcohol to sunlight is $UO_2(NO_3)_2$. J. F. S.

The Relation between Uranium and Radium. VII. Frederick Soddy (*Phil. Mag.*, 1919, [vi], **38**, 483—488. Compare Soddy and Hitchins, A., 1915, ii, 726).—The subsequent growth of radium in the old uranium preparations, since they were last tested in 1915, has confirmed the earlier result that the growth is proceeding according to the square of the time, and that the product of the two periods of average life of ionium and radium is, to an accuracy of some 5%, 237,500,000 years. Assuming the period of radium to be 2375 years, that of ionium is 100,000 years. It is not to be expected that this period will be determined with much greater accuracy, as the result of subsequent measurements upon these preparations. F. S.

Electrical Conductivity and Other Properties of Saturated Solutions of Copper Sulphate in the Presence of Sulphuric Acid. H. M. Goodwin and W. G. Horsh (*Chem. and Met. Eng.*, 1919, **21**, 181—182).—The specific electrical conductance at 25° of saturated solutions of copper sulphate contain-

ing sulphuric acid from 0·15 to 3·6 equivalents per litre has been determined, using the customary Wheatstone bridge arrangement with alternating current. The solutions were rotated in a constant temperature bath and the measurements continued until constant, which indicated saturation. The constant of the conductivity cell was determined by measuring the conductivity of normal potassium chloride solution and a solution of sulphuric acid of maximum conductivity. The results, accurate to 0·5%, show that the conductivity increases, following a straight-line law with increasing concentration of sulphuric acid. The solubility of copper sulphate in the presence of sulphuric acid is determined by electro-analysis. The concentration of copper sulphate at the saturation point falls continuously with increase of concentration of sulphuric acid up to 4 equivalents per litre. The acid content of the solutions was determined by titrating with standard sodium hydroxide solution in the presence of copper sulphate, using methyl-orange as an indicator. The density of the solutions was measured by means of a Mohr-Westphal balance. The density first falls with increasing sulphuric acid content and then increases rectilinearly with a minimum at about 0·5 equivalent per litre. T. H. B.

Applicability of the Precipitated Silver–Silver Chloride Electrode to the Measurement of the Activity of Hydrochloric Acid in Extremely Dilute Solution. G. A. Linhart (*J. Amer. Chem. Soc.*, 1919, **41**, 1175—1180).—Measurements of the *E.M.F.* of cells of the type $Ag, AgCl|HCl|H_2Pt$ have been carried out for concentrations of hydrochloric acid varying between 0·04826*N* and 0·000136*N*. The cell was made up in a single vessel, consisting of a bulb of about 1200 c.c. capacity fitted with fairly narrow tubes at the top and bottom. The bottom tube contained the silver–silver chloride electrode, and here a current of hydrogen entered just above the electrode; the top tube contained the hydrogen electrode of iridium coated platinum, and above the electrode was an exit tube for the hydrogen. The silver–silver chloride electrode consisted of a layer of fine-grained electrolytic silver covered with a layer of precipitated silver chloride. After filling, the cell was placed in a thermostat and kept at a temperature of 25° ± 0·01° for three to four days to come to equilibrium, and then the *E.M.F.* measurements were made over a considerable period of time until constant values were obtained. The following values of the *E.M.F.* for a hydrogen pressure of 1 atm. are obtained: HCl, 0·04826*N*, 0·3874 volt; 0·00965*N*, 0·4658 volt; 0·004826*N*, 0·5002 volt; 0·001000*N*, 0·5791 volt; 0·000483*N*, 0·6161 volt; 0·000242*N*, 0·6514 volt; and 0·000136*N*, 0·6805 volt. The *E.M.F.* is calculated to molecular concentration of hydrogen and chloride ions on the assumption of complete ionisation; these values extrapolated at infinite dilution yield the value 0·2234 volt, from which the degree of dissociation is calculated for each dilution. J. F. S.

Transport Number of Chromic Ions in Violet Chloride Solutions. Karl Hopfgartner (*Monatsh.*, 1919, **40**, 259—269).—The transport number of the chromic ion in hydrochloric acid solu-

tions of violet chromic chloride has been determined by the Hittorf method. The determinations were effected with solutions of three concentrations (1·00, 0·32, and 0·075 equivalent). The transport numbers found were 0·318±0·005, 0·357±0·003, and 0·414±0·005 respectively, which extrapolate to the value 0·446 for the concentration zero, and lineally extrapolate to 0·430. From these values the mobility of the chromic ion is estimated by various methods as 53, 49·5, and 46·3, and of these the first value is probably too high. The results indicate that the chromic ion is surrounded by a fairly large water sheath, although the various methods of calculating the magnitude of this give results which vary considerably.

J. F. S.

Anodic Peroxidation of Manganese in an Acid Medium in Presence of Silver Salts. Armando Rusconi (*Arch. farm. sper. sci. aff.*, 1919, **27**, 94—96).—When 30% sulphuric acid containing a small proportion (0·05%) of manganous sulphate is electrolysed in a U-shaped voltameter with a potential difference of 5—6 volts, the formation of traces of permanganic acid at the anode is observable after a few minutes. If, however, the solution contains also a few drops of saturated silver sulphate solution, the formation of permanganic acid at the anode is immediate and rapid. Similar results are obtained if the sulphuric acid is replaced by concentrated sodium hydrogen sulphate solution (compare Marshall, A., 1901, ii, 156; Scagliarini and Casali, A., 1913, ii, 181).

T. H. P.

Flowing Metal Vapour Arcs. Emil Podszus (*Zeitsch. Elektrochem.*, 1917, **23**, 179—181).—A metallic vapour arc is described which will burn steadily and continuously in any atmosphere. The lamp consists of a large globe of glass or quartz open at the bottom and fitted with a narrow exit tube at the top. The wide opening at the bottom stands in an iron dish containing mercury, and through the bottom of which are three openings. A narrow glass tube for admitting gas passes through the first; the second opening admits the cathode vessel, and the third the anode vessel. The cathode vessel is made of iron, and down the middle of it a tube of boron nitride passes; covering the top of the cathode is a plate of tungsten perforated by a narrow opening in the centre. The object of the boron nitride tube and the tungsten plate is to stabilise the arc and to prevent fluctuations of the mercury or amalgam which constitutes the cathode. The anode is a tungsten rod. The arc is struck by lowering the anode until it touches the cathode and then drawing it away. The arc produced is a thin, quiet flame, which is affected in colour by the gases in the globe and by the metal used as cathode. In hydrogen the light is greenish-white; in nitrogen bluish-white. All compound gases introduced into the arc were reduced; thus the solid element was obtained from boron trichloride and titanium tetrachloride, whilst calomel was also produced.

J. F. S.

A New Method for the Rapid Determination of Critical Temperatures. Application to Carbonyl Chloride. L. HACKSPILL and MATHIEU (*Bull. Soc. chim.*, 1919, **25**, 482—485).—A simple apparatus for the determination of critical temperatures consists of a cylinder of aluminium or copper about 25 cm. long and 5 cm. in diameter wound throughout its entire length with nickel wire, by which it is heated electrically. The liquid to be examined, contained in a thick glass tube, is placed in a hole in the axis of the cylinder, and can be viewed through a longitudinal slit in the cylinder. A second hole parallel to the first is provided for a thermometer. The critical temperature of carbonyl chloride was found to be 183±0·5° with this apparatus.

E. H. R.

The Critical Temperature as a Single Function of the Surface Tension. II. MAURICE PRUD'HOMME (*J. Chim. Phys.*, 1919, **17**, 325—328. Compare this vol., ii, 183). The author deduces, on theoretical grounds, the equation, previously put forward (*loc. cit.*), connecting the surface tension with the critical temperature. The relationship is verified in the case of a number of organic liquids.

J. F. S.

The Equation of State of Ethyl Formate. E. ARIÈS (*Compt. rend.*, 1919, **169**, 602—605).—The equation of state of ethyl formate, like that of ethyl acetate (compare this vol., ii, 360), satisfactorily represents the thermal properties of this fluid, except in so far as concerns the heat of vaporisation and the density of the vapour over a temperature range extending from the critical temperature to 35° below it.

W. G.

Standardisation of the Sulphur Boiling Point. E. F. MUELLER and H. A. BURGESS (*J. Amer. Chem. Soc.*, 1919, **41**, 745—763).—The boiling point of sulphur as a standard temperature has been investigated and the conditions under which it should be determined examined. The suggestion that the reflecting power of the inner surface of a radiation shield may influence the temperature assumed by a resistance thermometer is confirmed. A number of shields, both of glass and porcelain, have been examined, and several satisfactory forms are described. The influence of the type of boiling apparatus on the observed temperature is found to be very small. The presence of 0·05% of arsenic in the sulphur has no effect on the boiling point, but 0·10% raises the boiling point 0·02°, 0·05% of selenium, together with 0·10% of arsenic, raises the boiling point 0·08°, and 0·10% of arsenic and 0·10% of selenium raises the boiling point 0·09°. The boiling point of pure sulphur at 760 mm. pressure is 421·73°. The vapour pressure over the range 700 mm. to 800 mm. has been redetermined, and from these values an equation for calculating the boiling point at various pressures is deduced. This has the form $t=444{\cdot}60+0{\cdot}0910(p-760)-0{\cdot}000049(p-760)^2$. A résumé of the conditions to be observed in determining the boiling point of sulphur for standardisation purposes is appended to the paper.

J. F. S.

Determination of Boiling Points of Solutions. F. G. Cottrell (*J. Amer. Chem. Soc.*, 1919, **41**, 721—729).—A modified boiling-point apparatus is described for solutions whereby the conditions obtaining in the determination of the boiling point of pure liquids are imitated. In the present method, the Beckmann thermometer is placed in the vapour phase and the bulb coated with a thin film of the boiling liquid. The coating of the bulb with the boiling solution is effected by means of a narrow glass tube, which is placed in the liquid; this tube is funnel-shaped at the bottom and sealed at the top, but with a lateral hole just above the bulb of the thermometer. When the liquid boils, bubbles of vapour pass up the tube and carry boiling liquid into a cup through a loosely fitting opening in which the stem of the thermometer passes, the liquid flows over the bulb, and slowly drips back into the solution. It is claimed that this arrangement entirely removes errors due to superheating and yields accurate results extremely readily. J. F. S.

Laws of Concentrated Solutions. VI. The General Boiling-point Law. Edward W. Washburn and John W. Read (*J. Amer. Chem. Soc.*, 1919, **41**, 729—741).—The boiling points of concentrated solutions of naphthalene and diphenyl in benzene have been determined by means of the Cottrell boiling-point apparatus (preceding abstract). In the determinations, two pieces of apparatus were used, in one of which the pure solvent was kept continually boiling, and in the other the solution, so that the elevation of the boiling point was read directly and was independent of slight pressure changes. The apparatus was further modified by the addition of a side-tube, from which quantities of the solution were extracted for analysis. In the present case, the analysis consisted in determining the density of the solution at 25° and calculating the composition by means of an empirical equation connecting density and composition. The boiling-point law for ideal solutions and the connexion between the boiling-point elevation and the barometric pressure are considered. It is also shown how the molecular weight of a dissolved substance which undergoes solvation may be calculated from the elevation of the boiling point. J. F. S.

Molecular-weight Determination by Direct Measurement of the Lowering of the Vapour Pressure of Solutions. Robert Wright (T., 1919, **115**, 1165—1168).

The Evaporation of Concentrated and Saturated Solutions of Ammonium Nitrate, Vapour Pressures, Heats of Solution, and Hydrolysis. E. B. R. Prideaux and R. M. Caven (*J. Soc. Chem. Ind.*, 1919, **38**, 353—355T).—The vapour pressures of 47·8%, 60·4%, and saturated solutions of ammonium nitrate have been measured between 40° and 100°. In 60·4% solutions, which are about saturated at the ordinary temperature, the pressure still rises rapidly with rise of temperature, but the

pressures of saturated solutions are low, being no more than 17 cm. at 100°. The heats of evaporation, calculated from the vapour pressures, are, in the case of unsaturated solutions, about 50 cal. lower than that of water at the same temperature, and appear to reach a maximum at some temperature between 60° and 70°. The maximum is more pronounced with saturated solutions, occurring at about 60° with a latent heat of 400 to 450 cal.

When ammonium nitrate solutions are evaporated in contact with iron, there is considerable loss of ammonia and corrosion of the iron by the hydrolytic nitric acid. In acid-resisting vessels or vessels of aluminium, the loss of ammonia through hydrolysis is almost entirely obviated. E. H. R.

Improved Apparatus for the Estimation of Vapour Pressures. Allan Morton (*J. Soc. Chem. Ind.*, 1919, **38**, 363—364T).—Difficulties having arisen in the determination of the vapour pressures of certain organic liquids on account of the solvent action of these liquids on the lubricants employed for the stopcocks, an apparatus was devised in which taps were entirely avoided. The apparatus took the form of a U-shaped barometer with a bottom mercury reservoir. To the top of each barometer tube was fused a capillary tube, which was bent downwards with its end dipping into a mercury cup. The mercury having been thoroughly cleaned and dried, a sample of the liquid of which the vapour pressure was to be determined was placed in one of the two mercury cups, and, by suitable manipulation of the bottom reservoir, drawn up into one of the arms of the barometer. The difference between the mercury levels in the two arms was a measure, of course, of the vapour pressure. E. H. R.

The Vapour Pressures of Mixtures of Ether and Sulphuric Acid. Alfred W. Porter (*Trans. Faraday Soc.*, 1919, **14**, 280).—A correction to some remarks made by the author in a discussion on a paper by F. H. Campbell (A., 1916, ii, 83). E. H. R.

Use of Coal as a Substitute for Talcum to Induce Rapid Boiling. E. C. Kendall (*J. Amer. Chem. Soc.*, 1919, **41**, 1189—1190).—Small, compact pieces of anthracite serve excellently for bringing about rapid boiling of liquids and solutions, and also for preventing the bumping in Kjeldahl flasks. Powdered anthracite has not the same action, and anthracite which has been kept in water for some time loses its efficacy, but after baking for some time the efficacy is regained. J. F. S.

The Occlusion of Gases by Metals. Introductory Address to General Discussion. Sir Robert Hadfield (*Trans. Faraday Soc.*, 1919, **14**, 173—191).—A historical account of the subject, with special reference to the effect of occluded gases in steel castings. A bibliography is appended. E. H. R.

General Remarks on Occlusion of Gases in Metals. Alfred W. Porter (*Trans. Faraday Soc.*, 1919, **14**, 192—197).—The term "occlusion" probably covers a number of different phenomena which may take place either singly or in conjunction. These can be enumerated under six heads: first, chemical combination of gas with metal, for example, hydrogen with sodium, potassium, or palladium; secondly, simple solid solution, either separately or in conjunction with the first; thirdly, solid solution in contiguous phases; fourthly, solution accompanied by surface adsorption; fifthly, surface condensation under molecular forces, unaccompanied by solution; sixthly, inclusion, as when large or minute bubbles become entangled in the molten, viscous mass. The work of earlier investigators on occlusion, particularly the occlusion of hydrogen by palladium, is discussed from the point of view of this classification of the phenomena. The influence of condensed gases on the Volta effect is also discussed. E. H. R.

The Physical Properties of Metals as Affected by their Occluded Gases. Cosmo Johns (*Trans. Faraday Soc.*, 1919, **14**, 198—201).—To explain the profound effect of occluded gases on the physical properties of metals, for instance, the rendering brittle of iron or copper by hydrogen, the following theory is proposed. As a working hypothesis, it is assumed that hydrogen is soluble in the molten metals, but insoluble in the solid, and the theory is adopted that the tenacity of solid metals and the strength of the crystal boundaries are due to the presence of amorphous material, that is, an under-cooled liquid, which serves to cement the crystal grains which compose the solid mass. This intercrystalline matter must contain more hydrogen in solution than the solid metal can hold, and it is therefore at the crystal boundaries that the change in properties occurs, and the brittleness of the whole mass is explained. Relatively small quantities of gas dissolved in the intercrystalline material might thus cause profound changes in the properties of the metal.

The carbon monoxide and carbon dioxide found occluded in steel are probably formed by interaction of dissolved oxide of iron and carbon at the particular temperature when iron oxide, being thrown out of solution as freezing progresses, becomes concentrated in the mother liquor between the growing crystals and reacts with the carbon which has not suffered the same concentration. The gases would thus become concentrated in the intercrystalline layers, and would have the same effect as the hydrogen in copper and iron. Such data as are available on the physical properties of metals or alloys all refer to metals containing unknown quantities of occluded gases, which may profoundly modify their properties, and consequently knowledge of the properties of pure metals, if such can be obtained, is lacking. E. H. R.

Theories of Occlusion: the Sorption of Iodine by Carbon. J. W. McBain (*Trans. Faraday Soc.*, 1919, **14**, 202—212).—The term "sorption" is employed to include the phenomena of adsorp-

tion, absorption or true solid solution, and chemical reaction, all of which may accompany the fixation of a gas by a solid, and the occlusion of gases by metals is considered as a special instance of the process of sorption. The three processes involved in the phenomenon of sorption differ widely in their time relationships. True adsorption is nearly instantaneous, whilst absorption should obey Fick's diffusion law, commencing with a very high velocity for the first few moments and rapidly falling off with time. Chemical reaction may show the most varied time relationships, since it often proceeds vigorously in surface films as well as in solid solution. Since the occlusion of gases is hastened by rise of temperature, it is reasonable to conclude that the phenomena involved are largely those of diffusion, that is, of absorption rather than adsorption, whilst chemical reaction may play a prominent part.

It was shown by Davis (T., 1907, **91**, 1666) that the sorption by carbon of iodine dissolved in benzene, toluene, and other solvents consists of a surface condensation and a diffusion into the interior. The surface condensation is nearly instantaneous, whilst the diffusion proceeds for weeks or months. After an interval of eleven years, the experiments set up by Davis have been re-examined, and the sorption due to the slow diffusion of the iodine into the charcoal is found to be still continuing. Fresh experiments extending over four years have also confirmed Davis's results. E. H. R.

Balanced Reactions in Steel Manufacture. ANDREW MCCANCE (*Trans. Faraday Soc.*, 1919, **14**, 213—223).—A discussion of the equilibrium conditions in the open-hearth furnace during the manufacture of steel. The distribution of ferrous oxide between the steel and the slag and the influence of the furnace gases are particularly considered. E. H. R.

A Few Suggestions on the Theories of Occlusion of Gases by Metals. J. H. ANDREW (*Trans. Faraday Soc.*, 1919, **14**, 232—239).—From a consideration of the experimental evidence available, it is concluded that the occlusion of hydrogen by palladium is dependent on the presence of the active, amorphous form of the metal. Palladium in the crystalline state, free from contamination by the amorphous phase, is inactive towards hydrogen in the cold, but can be rendered active by continually pumping in and extracting gas from the metal, this treatment giving rise to the amorphous form. An amorphous layer of the metal will act as a vehicle for conveying the gas into the crystalline metal, the adsorbed layer of gas acting as a layer of extreme concentration and exerting the same effect as a high external pressure. In the occlusion of hydrogen by iron, the amorphous phase, in this case the intercrystalline cement, probably plays a prominent part. For instance, when a piece of wrought iron is immersed for some time in a saturated solution of sodium hydroxide at 100°, the mass becomes brittle, because the gas is absorbed

more rapidly in the amorphous intercrystalline layers than by the crystals themselves, and the expansion of these layers forces the crystals apart and weakens their cohesion. After remaining longer in the sodium hydroxide, the iron loses its brittleness, because the hydrogen gradually diffuses into the crystals from the intercrystalline cement. Electrolytic iron, being already saturated with hydrogen, is unaffected by sodium hydroxide. It is concluded that diffusion and occlusion are more or less identical, and can be explained by simple physical laws without reference to chemical combination. E. H. R.

Solutions. A. Reychler (*J. Chim. Phys.*, 1919, **17**, 209—265).—A theoretical paper in which many of the properties of solutions are considered. On the basis of Perrin's value of N, the Avogadro number, it is calculated that the mean kinetic energy of one molecule at 0° is $0{\cdot}5 \times 10^{-13}$ ergs, and that the charge e of one electron is $4{\cdot}2 \times 10^{-10}$ electrostatic units. An explanation of the mechanism of osmotic pressure is evolved, and a method of interpreting certain anomalies observed in osmotic pressure values is indicated. The author has developed the formulæ for calculating molecular weights from boiling-point elevations and freezing-point depressions on the basis of the vapour pressure formula. The nature of ionisation is considered, and it is shown that the ionic equilibrium is a condition of balance between the disruptive forces of the water and the attractions of the ions for one another, which, being of an electrical character, are never entirely eliminated, since they can act over a distance. A connexion is established between ionisation and an adsorption phenomenon. The reasons for the variation of the index in the dissociation laws of Storch and Noyes are considered. J. F. S.

Unique Case of a Liquid that Exhibits a Minimum Solubility in an Unstable Region. Marston Taylor Bogert and Jacob Ehrlich (*J. Amer. Chem. Soc.*, 1919, **41**, 741—745).—On cooling a clear solution of the monohydrate of 3:5-dimethoxyacetophenetidide in boiling water, there appeared a cloud of minute drops, which disappeared on further cooling, with the formation of a clear solution; from this, on continued cooling, white crystals eventually separated. To ascertain the nature of this behaviour, the solubility of this compound has been determined over the temperature range 21·8—173·6°. It is shown that the solubility increases with rise of temperature up to 87·5°, when the solid in contact with the solution melts. The solubility of the liquid hydrate increases more rapidly with further rise of temperature. Below 87·5°, the solubility of the liquid hydrate decreases with falling temperature until a point somewhere between 68·5° and 58·1° is reached, when it again increases. Hence the liquid hydrate has a minimum solubility at about 63°. The following solubilities in molecular percentages are recorded. (1) The solid hydrate: 21·8°, 0·010; 39·4°, 0·020; 57·0°, 0·046; 69·5°, 0·076; 72·8°, 0·091; 77·1°, 0·120; 80·2°, 0·151; 84·2°, 0·203; 86·0°, 0·237;

86·9°, 0·257. (2) The liquid hydrate: 35·6°, 0·301; 45·6°, 0·257; 58·1°, 0·237; 68·5°, 0·237; 84·3°, 0·257; 99·8°, 0·303; 111·1°, 0·361; 118·4°, 0·407; 129·2°, 0·499; 173·6°, 2·041. J. F. S.

Intermediate and Complex Ions. V. The Solubility Product and Activity of the Ions in Bivalent Salts. William D. Harkins and H. M. Paine (*J. Amer. Chem. Soc.*, 1919, **41**, 1155—1168. Compare A., 1917, ii, 77).—In previous papers (*loc. cit.*) it is shown that salts of tri-ionic and higher types ionise in steps and give, even in 0·1*N*-solutions, a large number of intermediate ions. In the present paper, the ionisation of salts composed of a bivalent cation and anion are considered. For this purpose, the solubility of calcium sulphate in water, and in solutions of copper sulphate, magnesium sulphate, and potassium nitrate, has been determined at 18° and 25°. The equivalent conductivity of various concentrations of the four salts and of the solutions of calcium sulphate in the others has been determined at the same temperatures, as well as the densities. The results show that the solubility relations of calcium sulphate when common ions are added are very similar to those of the higher type salts. This indicates the probability that complex ions, such as $Ca(SO_4)_2''$ and $Ca_2SO_4^{\cdot\cdot}$ are present in the solutions. These complex ions differ from what are usually considered under this title, since they are present to a considerable extent in dilute solutions, so in this sense they are more like intermediate ions. If it is assumed that such complex ions are absent, the solubility product, calculated on this basis, is found to increase with great rapidity as the concentration increases; thus, if the total ion concentration increases from 0·02*N* to 0·10*N*, the solubility product is trebled, so, if only simple ions are present, this activity decreases very rapidly with an increase in concentration. On the other hand, the solubility found for the un-ionised part, on the basis of this assumption, remains much more constant than in the case of uni-univalent salts. The change in the slope of these curves is in the direction which is to be expected if complex ions are present. The percentage concentration of such complexes is much higher in copper sulphate solutions than in magnesium sulphate solutions at the lower concentrations. J. F. S.

Reciprocal Solubility of Mixtures of Water, Alcohol, and Ether. A. Boutin and A. Sanfourche (*Bull. Soc. chim.*, 1919, [iv], **25**, 458—463).—The solubility of water in ether varies but little with temperature, but that of ether in water falls from 12·2% at −3·3°, the freezing point of water saturated with ether, to 4·0% at 35°. By adding one constituent to mixtures of the other two of known composition at 15° until two layers were just formed or just disappeared, limiting values were obtained for a series of ternary mixtures of varying composition. The results are conveniently plotted on a triangular diagram, each corner representing 100% of one constituent. A curve is obtained dividing the triangle into two zones, the one representing homogeneous and the other

heterogeneous mixtures. By drawing tangents to the curve from the points representing pure ether and pure water, the homogeneous zone is divided into six areas. One of these represents mixtures which cannot be made heterogeneous by addition of one constituent; two represent those which can only be made heterogeneous by addition of ether; two others represent those which can only be made heterogeneous by addition of water; whilst the last area represents mixtures which can be separated into two layers by either water or ether. No homogeneous mixture can be made heterogeneous by addition of alcohol alone. E. H. R.

Crystal Lattices and Bohr's Atom Model. L. Vegard (*Ber. deut. physikal. Ges.*, 1919, **21**, 383—385).—A short criticism of a paper by Born and Landé (this vol., ii, 188), in which the author states that some of the views expressed in the paper, and others attributed to Sommerfeld (A., 1918, ii, 303) were in reality put forward by him at an earlier date (A., 1918, ii, 93, 94, 144), and in consequence he claims priority. J. F. S.

Crystal Lattices and Bohr's Atom Model. M. Born and A. Landé (*Ber. deut. physikal. Ges.*, 1918, **21**, 385—387. Compare preceding abstract).—An answer to Vegard's criticism (*loc. cit.*), in which the authors allow the priority claim in some respects, but maintain their own in others. J. F. S.

An Experiment Relating to Atomic Orientation. T. R. Merton (*Phil. Mag.*, 1919, [vi], **38**, 463—464).—On the two assumptions, first, that the axes at right angles to the planes of the rings of electrons in the atom are orientated in a regular manner in a crystal structure, and, secondly, that the direction of expulsion of α- and β-particles from a radioactive atom is also related in some regular manner to this atomic axis, there should be a difference in the α- and β-activities of different faces of certain crystals of radioactive substances. The α-activities of three different faces of large crystals of uranium nitrate have been tested and found to be the same within the error of measurement, so showing that at least one of the two assumptions is incorrect. It is considered the more probable that the α-rays are shot out of the nucleus without regard to the orientation of the atomic axis. F. S.

Colloid Chemistry and its General and Industrial Applications. Second Report. F. G. Donnan, W. C. M. Lewis, E. F. Armstrong, Adrian J. Brown, C. H. Desch, E. Hatschek, H. R. Procter, W. Ramsden, A. S. Shorter, H. P. Stevens, and H. B. Stocks (*Rep. Brit. Assoc.*, 1918, 1—172).—The present report consists of articles on the following subjects: (i) Peptisation and precipitation (pp. 15), Wilder D. Bancroft; (ii) Emulsions (pp. 5), E. Hatschek; (iii) The Liesegang phenomenon (pp. 5), E. Hatschek; (iv) Electrical endosmose, I. (pp. 14), T. R. Briggs; (v) Electrical endosmose, II. (pp. 14), T. R. Briggs: this article deals with dewatering of peat and clay, electrical tanning, preservation of

timber, manufacture of bricks and electro-therapeutics; (vi) Colloid chemistry in the textile industries (pp. 18), W. Harrison; (vii) Colloids in agricultural phenomena (pp. 12), E. J. Russell; (viii) Sewage purification (pp. 15), E. Ardern; (ix) Colloid problems in dairy chemistry (pp. 22), W. Clayton; (x) Colloid chemistry in physiology (pp. 38), W. M. Bayliss; (xi) Administration of colloids in disease (pp. 18), A. B. Searle. J. F. S.

Vibration and Syneresis of Silicic Acid Gels. Harry N. Holmes, Wilford E. Kaufmann, and Henry O. Nicholas (*J. Amer. Chem. Soc.*, 1919, **41**, 1329—1336).—The tones produced by vibrating silicic acid gels have been investigated. Silicic acid gels were made which on tapping in thin-walled glass tubes produced a tone two octaves above middle *C*. Such gels vibrate as rigid solids, but tension is an important factor. That the gels are under considerable tension is shown by their great contraction in vaselined tubes. Contracted gels removed from vaselined tubes have a lower vibration frequency than similar gels adhering to the walls of tubes of equal diameter. Since vibration frequency varies inversely as the diameter of the gel column, tension must exert some influence on pitch. Vibration frequency varies directly as the concentration of silicic acid, increases with excess of mineral acid, and decreases with excess of organic acids. Syneresis (separation of aqueous solutions from highly hydrated gels) increases with increase in concentration of silicic acid, increases with excess of mineral acids, and decreases with excess of organic acids. For acid gels the factors which increase vibration frequency also increase syneresis. Vibration and syneresis are directly related to tension, but basic gels are abnormal in this respect. Syneresis varies directly as the free surface. When gels contract in vaselined tubes far more liquid separates than from equal volumes of gel in plain tubes to which the gel adheres. J. F. S.

Influence of the Age of Ferric Arsenate on its Peptisation. Harry N. Holmes and Paul H. Fall (*J. Amer. Chem. Soc.*, 1919, **41**, 713—717).—Determinations have been made of the amount of a 5*N*-solution of ferric chloride solution required to peptise 1·32 grams of ferric arsenate of various ages. The arsenate was prepared in bottles by adding 3 c.c. of 5*N*-ferric chloride solution to 17·6 c.c. of *M*/5-disodium arsenate solution and shaking vigorously for three minutes. The samples were then preserved, and after measured intervals were treated with ferric chloride solution and vigorously shaken until, by the trial method, the minimum quantity of ferric chloride required for peptisation was found. The experiments were made with ferric arsenate of ages varying up to fifty-six days. It is shown that the amount of ferric chloride required increases rapidly if the precipitate is allowed to age before peptisation—up to an age of one or two days. After this there is only a very small increase in the amount of ferric chloride needed even if the precipitate is kept a month before peptisation. The explanation of this behaviour is found in a decrease in hydration

of the precipitate—rapid during the first day and slow afterwards; also in the formation of larger aggregates with a consequent decrease in the external surface of the particles. Both influences retard diffusion of a solution of a peptising agent and greatly check the rate of peptisation. A few experiments, using ammonium hydroxide and sodium hydroxide as peptising agent, led to similar results. J. F. S.

Jellies [formed] by Slow Neutralisation. HARRY N. HOLMES and PAUL H. FALL (*J. Amer. Chem. Soc.*, 1919, **41**, 763—764).—Clear gels of ferric arsenate, peptised by ferric chloride, can be prepared by entirely filling a bottle with the sol, covering the neck with a piece of gold-beaters' skin, and placing in a tube attached to the neck 2 c.c. of *N*-ammonium hydroxide, 2 c.c. of saturated calcium hydroxide solution, or 2 c.c. of sodium acetate solution. The base diffuses through the membrane and neutralises the free acid slowly enough to allow of the formation of a perfect gel structure. J. F. S.

Calculation of the Equilibrium Constants in the Deacon Process. W. D. TREADWELL (*Zeitsch. Elektrochem.*, 1917, **23**, 177—179).—A theoretical paper, in which, making use of known data and the dissociation constants of water and hydrogen chloride, the author shows that the equilibrium constants of the Deacon process are given by the expression $\log K_p = 6034/T - 6{\cdot}972$. This expression is trustworthy between 300° and 1800°, and the values are nearly correct at temperatures in the region of the atmospheric temperature. J. F. S.

Influence of Substitution in the Components on the Equilibrium of Binary Solutions. VII. Binary Solutions Equilibria of α- and β-Naphthylamine respectively with Nitro-derivatives of Benzene. ROBERT KREMANN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 723—753. Compare this vol., ii, 275).—Fusion curves have been produced for the binary systems formed between α- and β-naphthylamine respectively and the three dinitrobenzenes, 2 : 4-dinitrotoluene, 1 : 3 : 5-trinitrobenzene, the three mononitrophenols, and 2 : 4-dinitrophenol respectively. It is shown that neither α- nor β-naphthylamine forms compounds with *o*-dinitrobenzene or *o*-nitrophenol; β-naphthylamine forms no compounds with 2 : 4-dinitrotoluene. Equimolecular compounds are formed between α-naphthylamine and *p*-dinitrobenzene (m. p. 81·8°), *m*-dinitrobenzene (m. p. 63·8°), 2 : 4-dinitrotoluene (m. p. 62°), *m*-nitrophenol (m. p. 56·3°), *p*-nitrophenol (m. p. 68·2°), and 2 : 4-dinitrophenol (m. p. 104·5°). A compound of unknown and undetermined composition is indicated in the system α-naphthylamine–trinitrobenzene. Equimolecular compounds are formed between β-naphthylamine and *p*-dinitrobenzene (m. p. 91°), *m*-dinitrobenzene (m. p. 53·3°), 1 : 3 : 5-trinitrobenzene (m. p. 161°), *m*-nitrophenol (m. p. 63·5°), *p*-nitrophenol (m. p. 81·5°), and 2 : 4-dinitrophenol (m. p. 72·3°). In the case of the

compounds with the dinitrobenzenes, the range of existence is greater for the compounds with α-naphthylamine than for those with β-naphthylamine. J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. VIII. ROBERT KREMANN and WILHELM CSANYI (*Monatsh.*, 1916, **37**, 755—760. Compare preceding abstract).—Fusion curves have been produced for the binary systems formed between β-naphthylamine and the three dihydroxybenzenes. It is shown that β-naphthylamine forms equimolecular compounds with resorcinol (m. p. 77·6°) and catechol (m. p. 81·3°). A compound (m. p. 141·7°) is formed between two molecules of β-naphthylamine and one molecule of quinol. J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. IX. A Comparative Determination of the Degree of Dissociation of some Additive Compounds in the Molten Condition. ROBERT KREMANN and GEORG GRASSER (*Monatsh.*, 1916, **37**, 761—774. Compare preceding abstracts).—The degree of dissociation of the equimolecular compounds, formed by naphthalene, α-naphthylamine, β-naphthylamine, and aniline with various other substances, has been calculated. The calculation was carried out by means of the formula of van Laar, $\alpha_0=(RT_0^2/Q_0)[x^2(1+x)]/[4(T_0-T)]$, in which T_0 is the melting point of the pure compound, α_0 the degree of dissociation, T is the melting point of a mixture of the compound and its components in a concentration x, and Q_0 is the total heat of fusion which is made up of the real heat of fusion q_0 and the heat of dissociation λ. Q_0 is determined experimentally from the initial direction of the fusion curve of the compound and an indifferent substance by means of the expression $(dT/dx)=-RT_0^2/(q_0+\alpha\lambda)=-RT_0^2/Q_0$. As indifferent substances, *p*-nitrotoluene and nitrobenzene were used in the experiments. The following values of α_0 were obtained: naphthalene–*m*-dinitrobenzene, 0·93; naphthalene–*p*-dinitrobenzene, 0·87; naphthalene–2 : 4-dinitrotoluene, 0·86; naphthalene–2 : 4-dinitrophenol, 0·83; α-naphthylamine–*m*-dinitrobenzene, 0·53; α-naphthylamine–2 : 4-dinitrotoluene, 0·58; α-naphthylamine–*m*-nitrophenol, 0·55; α-naphthylamine–*p*-nitrophenol, 0·56; α-naphthylamine–2 : 4-dinitrophenol, 0·28; β-naphthylamine–*m*-dinitrobenzene, 0·88; β-naphthylamine–*m*-nitrophenol, 0·55; β-naphthylamine–*p*-nitrophenol, 0·54; β-naphthylamine–2 : 4-dinitrotoluene, 0·61; aniline–*m*-dinitrobenzene, 0·23; aniline–2 : 4-dinitrotoluene, 0·67; aniline–phenol, 0·44; and aniline–*m*-cresol, 0·10. J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XIX. The Binary Systems of Antipyrine with Phenols and their Derivatives. ROBERT KREMANN and OTFRIED HAAS (*Monatsh.*, 1919, **40**, 155—188. Compare this vol., ii, 275).—By means of melting-point curves, the binary systems, antipyrine and phenolic sub-

stances, have been investigated with the object, as in the previous communications, of ascertaining the influence of substitution on the tendency of organic substances to form molecular compounds. In the present papers, the systems antipyrine with phenol, salicylic acid, α-naphthol, β-naphthol, *o*-nitrophenol, *p*-nitrophenol, *m*-nitrophenol, 2:4-dinitrophenol, pyrogallol, catechol, quinol, and resorcinol have been examined and the fusion curves constructed. It is shown that an equimolecular compound is formed between antipyrine and salicylic acid, phenol, α-naphthol, and β-naphthol respectively. In the case of the nitrophenols, antipyrine, as in other cases, forms no compounds with *o*-nitrophenol, but with *p*-nitrophenol three molecular compounds are formed, namely, two molecules of antipyrine with one molecule of *p*-nitrophenol, and one molecule of antipyrine with one and two molecules, respectively, of *p*-nitrophenol. In the cases of *m*-nitrophenol, pyrogallol, and 2:4-dinitrophenol, only the melting-point curves of the pure components could be observed, owing to the extreme slowness of the crystallisation of the melt lying between them. There is little doubt that in these cases one or more molecular compounds exist, but they could not be obtained. Catechol forms three molecular compounds with antipyrine, one molecule of the phenol to one and two molecules of antipyrine respectively, and two molecules of the phenol to one molecule of antipyrine. In the case of quinol, two compounds are formed, two molecules of antipyrine to one and three molecules, respectively, of quinol. J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XX. The Binary Systems of Acenaphthene with some Nitro-derivatives of Benzene. Robert Kremann and Otfried Haas (*Monatsh.*, 1919, **40**, 189—204. Compare preceding abstract).—Fusion curves have been constructed for the binary systems formed between acenaphthene and the three dinitrobenzenes, 2:4-dinitrotoluene, the three nitrophenols, 2:4-dinitrophenol, and picric acid respectively. The systems acenaphthene–*o*-dinitrobenzene and acenaphthene–*p*-dinitrobenzene form no compounds, but simple eutectics; *m*-dinitrobenzene, on the other hand, forms an equimolecular compound (m. p. 70·1°). In the case of dinitrotoluene, an equimolecular compound is also formed (m. p. 57·5°). No compounds are formed between acenaphthene and the three nitrophenols, simple eutectics being formed in each case. An equimolecular compound is formed between 2:4-dinitrophenol and acenaphthene (m. p. 86°), and a similar equimolecular compound is formed between picric acid and acenaphthene (m. p. 151·5°).

J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXI. The Binary Systems of Trimethylcarbinol with Phenols and Amines respectively. Robert Kremann and Otto Wlk (*Monatsh.*, 1919, **40**, 205—236. Compare preceding abstract).—Fusion curves have

been constructed for the binary systems trimethylcarbinol and the three dihydroxybenzenes, α-naphthol, β-naphthol, pyrogallol, *p*-toluidine, the three phenylenediamines, α-naphthylamine and β-naphthylamine respectively. It is shown that two compounds are formed between catechol and trimethylcarbinol, namely, between two molecules of catechol and one molecule of the alcohol (m. p. 69·7°), and between two molecules of the alcohol and one molecule of catechol (m. p. 29°). In the case of resorcinol and trimethylcarbinol, two compounds are also formed, an equimolecular compound (m. p. 45·8°) and a compound between two molecules of the alcohol and one molecule of resorcinol (m. p. 47·3°). The volatility of trimethylcarbinol rendered the examination of the fusion curve with quinol incomplete, so that nothing can be said of any compounds which may be formed in this case. Pyrogallol, α-naphthol, and β-naphthol each form a single compound with trimethylcarbinol which melt at 56·2°, 1·0°, and 24° respectively. Trimethylcarbinol forms no compounds, but only simple eutectics with *p*-toluidine, *m*-phenylenediamine, and *p*-phenylenediamine. Two compounds are formed between trimethylcarbinol and β-naphthylamine, namely, a compound between two molecules of the amine and one molecule of the alcohol (m. p. 95·5°), and between one molecule of the amine and two molecules of the alcohol (m. p. 92°). In the case of α-naphthylamine, three compounds are formed, namely, between two molecules of the amine and one molecule of the alcohol (m. p. 29·5°), one molecule of the amine and two molecules of the alcohol (m. p. 24·1°), and between one molecule of the amine and six molecules of the alcohol (m. p. 16·0°). J. F. S.

Influence of Substitution in the Components on the Equilibrium in Binary Solutions. XXII. The Binary Systems Triphenylcarbinol with Phenols and Amines respectively. Robert Kremann and Otto Wlk (*Monatsh.*, 1919, **40**, 237—258. Compare preceding abstracts).—Fusion curves have been constructed for the binary systems triphenylcarbinol and phenol, α-naphthol, β-naphthol, quinol, catechol, resorcinol, *p*-toluidine, α-naphthylamine, and β-naphthylamine respectively. It is shown that phenol, α-naphthol, and β-naphthol form only simple eutectics, and no compounds with triphenylcarbinol. Triphenylcarbinol forms a single compound with two molecules of catechol (m. p. 82·0°) and with two molecules of quinol (m. p. 151·6°). In the case of resorcinol, a reddish-brown substance of high melting point separates from the mixture when the concentration of the mixture lies between 25% and 55% of triphenylcarbinol. This compound has not been further examined and is not a molecular compound. No molecular compounds are formed between triphenylcarbinol and *p*-toluidine, α-naphthylamine and β-naphthylamine, respectively, simple eutectics being formed in each case. J. F. S.

Interchange of Bases in Permutite. GERTRUD KORNFELD (*Zeitsch. Elektrochem.*, 1917, **23**, 173—177. Compare A., 1918, ii, 315).—The replacement of sodium in sodium permutite by silver, and the replacement of silver in silver permutite by potassium, barium, and ammonium have been studied. It is found that shaking permutite with solutions of the various salts for twenty minutes is sufficient to complete the interchange. In all cases except the replacement of silver by barium, the concentration of the solution has no effect on the amount of change. The change between sodium permutite and silver is represented by the equation $([Ag_P]/Na_P)^{1\cdot64} \times (Na_L/Ag_L) = 129$, the indices P and L denoting, respectively, permutite and solution. In the case of silver permutite and ammonium nitrate, the reaction is represented by $(Ag_P/[NH_4]_P)^{1\cdot67} \times ([NH_4]_L/Ag_L) = 37\cdot7$. The replacement of silver by potassium is given by the equation

$$(Ag_P/K_P)^{2\cdot17} \times (K_L/Ag_L) = \text{const.} = 9\cdot9,$$

and the replacement of silver by barium by the formula

$$1\cdot5 = (Ag_P/\sqrt{Ba_P})^{2\cdot8} \times (\sqrt{Ba_L}/Ag_L).$$

The various theories put forward to explain the above-mentioned interchange are discussed in the paper. J. F. S.

Wollastonite (CaO,SiO_2) and Related Solid Solutions in the Ternary System Lime–Magnesia–Silica. J. B. FERGUSON and H. E. MERWIN (*Amer. J. Sci.*, 1919, [iv], **48**, 165—189).—A continuation of work previously published (this vol., ii, 401). In the present paper, the solid phases of the ternary system lime–magnesia–silica are examined. The solid phases were obtained by preparing glasses of the desired composition and crystallising at low temperatures. The solids obtained were heated at various temperatures and the changes noted. The results confirm the earlier work with regard to the wollastonite–diopside solid solutions, namely, that wollastonite will take up a maximum of 17% of diopside to form solid solutions. The existence of solid solutions of pseudowollastonite–diopside containing a maximum of 16% of diopside is confirmed. A new compound, $5CaO,2MgO,6SiO_2$, is described. Solid solutions of åkermanite (or perhaps of an unstable compound, $3CaO,MgO,3SiO_2$) in both wollastonite and pseudowollastonite are shown to exist. The wollastonite solutions extend to a composition containing between 60% and 70% of åkermanite, and the pseudowollastonite solid solutions extend to a composition containing about 23% of the same compound. It is shown that an area exists in which the wollastonite–diopside, wollastonite–åkermanite, and wollastonite–$5CaO,2MgO,6SiO_2$ solid solutions are all capable of existence. The decomposition temperatures on this area between the 17% diopside solid solution and the compound $5CaO,2MgO,6SiO_2$ pass through a minimum. The compound $5CaO,2MgO,6SiO_2$ decomposes at 1365°, and the 17% diopside solid solutions at about 1340°, whilst pure wollastonite undergoes inversion at 1200°.

Further, the inversion temperatures and decomposition temperatures of the solid solutions of silica and the compound $3CaO,2SiO_2$ were studied. The results are discussed generally, and diagrams and models to represent the system are drawn. J. F. S.

Graphic Representation of Systems of the Form $a+b=c$ in Triangular Co-ordinates and a [Method of] Presentation of the Phase Rule. Wa. Ostwald (*Zeitsch. Elektrochem.*, 1919, **25**, 251—254).—A mathematical paper in which the representation of systems of the form $a+b=c$ on triangular co-ordinates is considered. The use of such a co-ordination system for the general representation of phase-rule problems is discussed. J. F. S.

Theory of Detonation. R. Becker (*Zeitsch. Elektrochem.*, 1917, **23**, 40—49).—The theory of detonation is developed mathematically, and from the equations deduced the following values are calculated, which are of the same order as the experimentally determined values: for a detonation temperature of 2000° with glyceryl trinitrate, a detonation pressure of 92,500 atms. is set up and the detonation proceeds through the mass with a velocity of 7230 metres per sec.; for 2500° the corresponding figures are 110,500 atm. and 7930 metres per sec. J. F. S.

Development of Atomism. I. M. Giua (*Gazzetta*, 1919, **49**, ii, 1—42).—A historical essay with the headings: Genesis of atomism; precursors of atomism in Greece; doctrine of the elements: Anaxagoras and Empedocles; the atomistic system: Leucippus and Democritus; Plato and Aristotle; atomism of Epicurus; atomistics in the poem of Lucretius; atomistics in the Middle Ages; Arabic atomism. T. H. P.

Harmony of the Atomic Weights. Eduard Schmiz (*Ber., Deut. pharm. Ges.*, 1919, **29**, 504—518).—The author calculates numerical relationships between the atomic weights of the elements. These relationships are the same as those which exist between the sides, hypotenuse, and radius of the inscribed circle of an isosceles right-angled triangle, and the radius of the circumscribed circle round the squares erected on the sides of the triangle. The ratios of the named lines are $\sqrt{2}/2:1:(\sqrt{2}-1)/2:\sqrt{5}/2$. Thus in twelve cases it is shown that the ratio of the atomic weights of pairs of elements in the same group of the periodic system is $\sqrt{5}:\sqrt{2}$; in nine other cases the ratio is $\sqrt{5}:\sqrt{5}-1$. In several cases contiguous elements in the same series exhibit the ratio $\sqrt{5}/2:(2\sqrt{2}-1)/2$. Other relationships of a similar character are also given. J. F. S.

Law of Multiple Proportions. E. Puxeddu (*Gazzetta*, 1919, **49**, i, 203—208).—The various forms in which the law of multiple proportions is expressed, including the new statement of this law by Balareff (A., 1918, ii, 15), are discussed. It is shown that the law,

usually illustrated by means of the oxides of nitrogen and by a few other inorganic and organic groups of compounds, possesses an intrinsic significance different from that commonly attributed to it, and that the new mode of enunciating it is a necessary consequence of various principles of general chemistry, and does not correspond exactly with the original enunciation. T. H. P.

Determination of Molecular and Atomic Weights; the Density of Gases under Normal Conditions and Critical Constants. J. J. VAN LAAR (*J. Chim. Phys.*, 1919, **17**, 266—328).—A critical consideration of the methods of calculating atomic and molecular weights of gases from purely physical data. It is shown that for the majority of gases, on the assumption that $v=\infty$, $a = a_c(e^{a/RT})/e^{a/RT_c})$ and $b = b_c(e^{a/RT})/(e^{a/RT_c})$, where $a = RT_c$. At 0° $RT_0=1$ and $a_0=(a_c)_\infty e^{RT_c-1}$ and $b_0=(b_c)_\infty . e^{RT_c-1}$. On reducing a_c and b_c of the volume v_c to the volume $v=\infty$, the values become $(a_c)_\infty = \phi a_c$ and $(b_c)_\infty = \phi b_c$, where ϕ is given by the expression $\phi=1+\epsilon T_c$, in which ϵ has a value 54×10^{-5} for substances with a critical temperature below 300° Abs. and 43×10^{-5} for substances with a critical temperature above 300° Abs. This difference may probably be expressed by an expression of the type $\phi=1+\epsilon T_c-\epsilon' T_c^2$. The value $\epsilon=43\times10^{-5}$ may, however, always be used, since the value of B_0 is nearly always relatively very small for substances with a critical temperature below 300° absolute, so that this value has little influence on the value of M. The function $e^{a/RT}$ often appears too large for diatomic gases, and in this case it may be retained if $a=\frac{1}{2}RT_c$ is employed. In the majority of cases where the critical temperature is above 300° $B_0=b_0-a_0=(b_c-a_c).e^{RT_c-1}\times(1+0{\cdot}00043T_c)$. In this formula b_c may be calculated from the expression $b_c=RT_c/8p_c$, and a_c from $a_c=RT_c\times b_c\times 27/8:\lambda$, where the correcting factor λ is obtained from the formula $\lambda=27/(8\gamma-1)[\gamma/(\gamma+1)]^2$ and $2\gamma=1+0{\cdot}038\sqrt{T_c}$. In the case of abnormal substances a_c and b_c may not be calculated by the above simple formulæ, but by means of much more complicated formulæ which are developed in the paper. The formulæ put forward are used to calculate the atomic weights of carbon, xenon, nitrogen, helium, hydrogen, neon, argon, and krypton from physical data, and yield values in excellent agreement with the accepted values.

J. F. S.

Single Deflexion Method of Weighing. PAUL H. M.-P. BRINTON (*J. Amer. Chem. Soc.*, 1919, **41**, 1151—1155).—To use this method, the balance is given a permanent overload on the left arm by screwing the adjusting nut on one end of the beam until, when the beam and pans are released, the pointer swings out 3 to 7 divisions to the right. The pan arrests must be so adjusted that there is no lateral vibration of the pans when released, and the method may not be used with balances in which the beam and pans are released by a single operation, such as the turning of a single

milled head or lever. In making a measurement after freeing the beam, the pans are released by a gentle, steady motion, the pointer swings out to the right, and the turning point of the single swing is taken as the zero of the balance. To obtain the weight of any object, it is counterbalanced by weights until on releasing the pans the pointer swings out to the same point. A number of readings made by the author and by students are given to show that exceedingly rapid weighing to within 0·1 mg. is possible by this method.

J. F. S.

Self-acting Mercury Pump. A. Stock (*Zeitsch. Elektrochem.*, 1917, **23**, 35—40).—A self-acting mercury pump, on the Toepler principle, is described, which permits the collection of the gases pumped off. The movable mercury reservoir is replaced by a strong three-necked bottle into which the foot of the pump enters. The mercury is raised by means of air or carbon dioxide under pressure until the pump is full, then by means of valves actuated by the mercury, the pressure is cut off and the mercury falls again. The pump has the advantage, in addition to the ease of operation, that the mercury does not become contaminated with impurities from rubber connexions between its two main parts. J. F. S.

Greaseless Valve for Gas Work. A. Stock (*Zeitsch. Elektrochem.*, 1917, **23**, 33—35).—A modification of the floating valve previously described (A., 1915, ii, 339) is given in the paper. This consists of a pair of narrow tubes ground to fit a constriction in each of two parallel tubes. On raising a mercury reservoir connected with the tubes the valves are raised and close the apparatus. The action is similar to that of the valve in a Toepler pump. Three forms of valve are described which are designed for use in working with gases which have chemical action on the lubricant used with glass taps. These valves are made of a porous material which will allow the passage of gases, but not of mercury, so that when the valve is in contact with mercury no gas may pass. The valves are fitted into the glass parts of apparatus by ground joints. These valves may be used in the production of high vacua, and they exhibit no tendency to absorb gases. They are rather slow in action; thus the pressure in a 1350 c.c. flask filled with air was reduced from 760 mm. to 391 mm. in five minutes, to 189 mm. in fifteen minutes, 73 mm. in thirty minutes, and to 0·0006 mm. in ten hours by means of a mercury pump fitted with a double valve of the type described. J. F. S.

Gas Washing and Absorption Apparatus. Fritz Friedrichs (*Zeitsch. angew. Chem.*, 1919, **32**, 252—256).—The author discusses the properties of some thirty different forms of gas-washing and gas-absorption apparatus which have been described since the first Woulfe's bottle was used for the purpose. He considers that only those forms which have a "serpentine" principle ensure complete washing or absorption of a gas under reasonable conditions.

W. P. S.

Simple Distillation and Extraction Apparatus. H. W. VAN URK (*Pharm. Weekblad*, 1919, **56**, 1301—1303).—A description, illustrated by a diagram, of a simple apparatus which may be used alternatively for direct distillation or extraction. W. S. M.

Inorganic Chemistry.

An Electrolytic Hydrogen Generator for the Laboratory. L. D. WILLIAMS (*J. Soc. Chem. Ind.*, 1919, **38**, 355T).—The cell consists of a filter flask of 250 c.c. capacity fitted with a cork carrying a straight tube 30 cm. long and 1·5 cm. wide. The anode is a strip of lead inside the tube 25 cm. long, the lower end as wide as possible, whilst the remainder is 1 cm. wide. The upper end is soldered to a copper lead which supports the electrode so that its lower end is 1 cm. above the bottom of the tube. The cathode is a strip of lead foil thin enough to pass between the cork and the neck of the flask without causing any leakage. The electrolyte consists of 20% sulphuric acid, and should nearly fill the flask when the exit is open. Such a cell will produce 7 c.c. of hydrogen per ampere per minute. The ideal plant for a small laboratory consists of ten cells run normally at 1 ampere, with a variable resistance, an ammeter, and purifying apparatus. The cell can also be used as a source of oxygen. E. H. R.

Physical Constants of Chlorine under the Action of Light. A. CAMPETTI (*Nuovo Cim.*, 1919, [vi], **17**, i, 143—158).—Experiment shows that the internal friction and the thermal conductivity of chlorine are not appreciably modified by the light from an arc lamp which has been passed through a dilute solution of copper sulphate to free it from most of the less refrangible radiations. The same is, contrary to the conclusions of Trautz (A., 1912, ii, 746), most probably the case with the thermal capacity, that is, the specific heat at constant volume, of the gas. The value of $\eta \times 10^7$ found for chlorine is 1328 at 15°. The thermal conductivity of chlorine is about 0·8 times that of air. T. H. P.

The Catalytic Oxidation of Ammonia. PAUL PASCAL and EUGÈNE DECARRIÈRE (*Bull. Soc. chim.*, 1919, [iv], **25**, 489—507).—Platinum was used as a catalyst in six different states of subdivision, varying from thin platinum foil cut into pieces and made into balls to platinised anhydrous magnesium sulphate. There is a certain minimum temperature for an appreciable velocity of oxidation varying with the physical state of the catalyst. This minimum temperature increases with the curvature of the surface of the catalyst, but is independent of the duration of contact and

of the concentration of the air–ammonia mixture. In every case there is a certain temperature and concentration range over which the maximum oxidation occurs, the yield diminishing outside these limits and becoming insignificant at 900°. In the case where balls of platinum foil were the catalyst, increasing the oxygen content of the air slightly increased the yield. The ammonia not converted into oxides of nitrogen is almost invariably lost as free nitrogen, but there are three exceptions where some of the ammonia passes through unchanged: (1) when the temperature is only about 320°; (2) when the alveolar industrial catalyst is used; (3) when the catalyst is a plug of very fine platinum wire or wool. [See, further, *J. Soc. Chem. Ind.*, 1919, November.] W. G.

Effect of Diminution of Pressure on the Fixation of Nitrogen as Nitric Oxide by means of the Electric Arc. E. Briner and Ph. Naville (*Helv. Chim. Acta*, 1919, **2**, 348—352).—As in the formation of ammonia (compare this vol., ii, 148, 190, 338), the optimum yield of nitric oxide from nitrogen–oxygen mixtures under the influence of the electric arc is given when the nitrogen is in excess, when the pressure is low, and when electrodes of certain metals are employed; iron and nickel behave normally, the optimum yield being then obtained with 50% of oxygen, whilst the displacement of the optimum towards the nitrogen-rich mixtures is most marked with platinum and less so with iridium and copper. The actual increases in the yield produced by lowering the pressure and by using excess of nitrogen are less pronounced than in the case of ammonia, but the dependence of the displacement of the optimum yield on a reaction localised in the neighbourhood of the electrodes is more apparent, and is shown only with short arcs and particularly with parallel electrodes. These results are in accord with Guldberg and Waage's law only if the active masses are represented by the concentrations of active particles, and not by the molecular concentrations of the two elements; such active particles are most probably the neutral atoms liberated by the dissociating action of the arc on the molecules. The favourable result obtained by use of excess of nitrogen is explained by the greater resistance to dissociation exhibited by nitrogen molecules. T. H. P.

Alkali Hypochlorites; Free or Combined Salts. Ed. Justin-Mueller (*J. Pharm. Chim.*, 1919, [vii], **20**, 113—115).—Reasons and evidence are adduced to show that alkali hypochlorites have the formula X_2OCl_2 or NaOCl,NaCl, the constituents in the latter formula being combined to form a single molecule. The similarity between the reactions of calcium hypochlorite and alkali hypochlorite favours the combined salt view, as does also the decomposition of calcium hypochlorite by sodium carbonate: $CaOCl_2 + Na_2CO_3 = Na_2OCl_2 + CaCO_3$. The reaction between a hypochlorite and sulphuric acid would be represented by the equation $Na_2OCl_2 + H_2SO_4 = Na_2SO_4 + Cl_2 + H_2O$, whilst the equation

$NaOCl + NaCl + H_2SO_4 = Na_2SO_4 + Cl_2 + H_2O$ would be representative of the reaction if the hypochlorite consisted of NaOCl.

W. P. S.

New Compound of Lime and Bromine and a Process for its Manufacture. John Stanley Arthur and Leonard Gibbs Killby (Brit. Pat., 131750).—A new bactericidal compound, $CaO,CaOBr_2,H_2O$, having properties similar to bleaching powder, but stable up to 100°, is produced by heating at 100° the red compound, $CaOBr_2,H_2O$, formed by acting on quicklime with bromine and water in the proportion of 100 grams of the former to 41 c.c. of bromine and 36 c.c. of water. During the heating, bromine and water are evolved, and the new compound remains as a pale yellow powder containing about 33% of available bromine. [See also *J. Soc. Chem. Ind.*, 1919, 843A.] G. F. M.

Some Chemically Reactive Alloys. E. A. Ashcroft (*Trans. Faraday Soc.*, 1919, **14**, 271—277).—Alloys of magnesium and lead containing from 5% to 50% of magnesium and 95% to 50% of lead when exposed to moist air rapidly absorb the whole of the oxygen present. The two metals form the compound Mg_2Pb, and the corresponding alloy, containing 19% of magnesium and 81% of lead, is the most reactive of the series. During the oxidation process, the alloy crumbles to a black powder, a mixture of magnesium hydroxide, $Mg(OH)_2$, and a hydrate of lead sub-oxide, $Pb_2(OH)_2$, being formed. These hydrates are stable when heated at 200°. The mixture is unaffected by further exposure to dry air, but in presence of water further oxidation occurs, the lead sub-oxide being oxidised to $Pb(OH)_2$. With the more reactive alloys, the action takes place in the cold, but with those containing upwards of 35% of magnesium, heat is necessary. The use of these alloys is suggested for removing the last traces of oxygen from gas mixtures, for instance, in the preparation of pure hydrogen for aircraft purposes.

When the alloys are boiled with water, oxidation occurs and free hydrogen is formed. The magnesium is oxidised rapidly, but the formation of lead sub-oxide takes place relatively slowly. When, however, the digestion with water is carried out under pressure at about 150°, the lead is completely oxidised to lead oxide and the theoretical quantity of hydrogen is liberated.

Alloys of magnesium and zinc are far less reactive. In fact, these alloys show greater resistance to oxidation than either magnesium or zinc alone (compare Grube, A., 1905, ii, 320).

E. H. R.

Thorium Lead. O. Hönigschmid (*Zeitsch. Elektrochem.*, 1917, **23**, 161—165).—After a discussion on the atomic weights and origins of the various lead isotopes, the author describes a series of experiments made to determine the atomic weight of the lead extracted from thorite from Ceylon. The method of analysis is the same as that previously described (A., 1914, ii, 653). Four

determinations were made of the ratio (Th)–$PbCl_2$:2Ag and four determinations of the ratio Th–($PbCl_2$):2AgCl. From the first set of measurements the value 207·77 is obtained, and from the second set the value 207·78. From both sets, the mean value 207·77±0·14 is calculated as the atomic weight of lead from this source. The present value is entirely in agreement with the value determined by Soddy (T., 1914, **105**, 1402) by an indirect method. Assuming the stability of the two isotopes Ra(G) and Th(E), the author calculates that these two substances are present in the ratio 20:7, or that the lead from thorite consists of 8·9% of uranium-lead and 91·1% of thorium-lead. J. F. S.

Thallium Selenides. Luigi Rolla (*Atti R. Accad. Lincei*, 1919, [v], **28**, i, 355—359).—According to both Pélabon (A., 1907, ii, 688) and Murakami (A., 1916, ii, 34), thallium and selenium form three compounds, the former giving to them the formulæ Tl_2Se, TlSe, and Tl_2Se_5, and the latter Tl_2Se, TlSe, and Tl_2Se_3. The author's attempts at thermal analysis of this system lead to discordant results, the inapplicability of this method depending on the slowness of the reaction involved or on its inconsiderable heat effect. The more sensitive method, consisting in tracing the variation of the solution tension with change of the composition, has therefore been employed, the results obtained excluding the existence of the third thallium selenide, for which different formulæ were given by Pélabon and Murakami. T. H. P.

Rare Earths. IX. Atomic Weight of Yttrium. III. H. C. Kremers and B. S. Hopkins (*J. Amer. Chem. Soc.*, 1919, **41**, 718—721).—The atomic weight of yttrium has been determined by the silver chloride method. The yttrium compound was purified by the sodium nitrite precipitation method (A., 1917, ii, 34), and the product converted into oxalate. The oxalate was ignited in a platinum dish and the oxide dissolved in redistilled nitric acid. The solution was filtered and diluted with 2 litres of "conductivity water" in a Jena flask, and treated with ammonia gas. The precipitated hydroxide was washed by decantation, dissolved in nitric acid, and reprecipitated with oxalic acid. The oxalate was again ignited, and the whole process of purification repeated. The final oxide was moistened with water, and hydrogen chloride passed over until all had dissolved, and, after filtering, the solution was stored in a quartz flask. The method of dehydrating, fusing, and weighing the anhydrous chloride was the same as previously described (*loc. cit.*). The anhydrous yttrium chloride was dissolved in a small quantity of water in a small quartz flask, and the solution transferred to a 5-litre glass bottle, diluted with 2 litres of water, and treated slowly with continuous shaking with the same volume of silver nitrate solution containing the calculated amount of silver nitrate. The bottle and contents were then placed in a shaking machine and shaken for twelve hours. The precipitate was allowed to settle, and the solution tested in a nephelometer for an excess of either chloride or silver ions. Additions of a standard solution

of either silver nitrate or sodium chloride were made until equivalence was obtained, and the solution again shaken for several hours. The whole process was carried out in a dark-room. The precipitation was effected in the above manner because earlier experiments had shown that equilibrium was only slowly attained, and dilute solutions with shaking were important factors in reaching a satisfactory end-point. Experiments were made with seven samples, and from the ratio $3Ag : YtCl_3$ the atomic weight of 89·33 was obtained, the extreme values being 89·30 and 89·34.

J. F. S.

Reducing Action of Manganous Oxide. V. Macri (*Boll. chim. farm.*, 1919, **58**, 201—202).—Manganous sulphate completely precipitates the silver from a hot ammoniacal silver nitrate solution. The white precipitate formed by addition of the manganous salt to ammoniacal mercuric nitrate solution turns grey and then brown on boiling, and, after treatment with sulphur dioxide solution or an acidified solution of a sulphite, leaves a heavy, brownish-grey, pulverulent deposit, which is not dissolved by dilute nitric acid, but is readily attacked by the concentrated acid, with formation of nitrous fumes. When an ammoniacal solution of copper and manganous sulphates is boiled, cuprous oxide is precipitated; the supernatant, colourless liquid gradually becomes blue in the air. Addition of ammonia to a solution containing a cobalt and a manganous salt yields a precipitate of manganous hydroxide which gradually becomes brown, not, however, by direct reduction of the cobalt oxide, since the latter first undergoes peroxidation in the air, and then gives up its oxygen to the manganese, especially on shaking. No tests were made with gold or platinum, but the hydroxides of other metals are not oxidised by manganous salts.

T. H. P.

Corrosion of Metals, especially Rusting of Iron. F. Goudriaan (*Chem. Weekblad*, 1919, **16**, [40], 1270—1285).—The conditions governing the corrosion of metals, especially the rusting of iron, have been investigated by the author. In pure, air-free water the process is purely electrolytic. When the concentration of the $Fe^{\cdot\cdot}$ ions in the solution is $1{\cdot}2 \times 10^{-6}$ gram-mols. per litre, action ceases. The addition of oxygen produces a very marked effect; the oxidation of the ions gives rise to a fresh *E.M.F.*, and corrosion will continue unless interrupted by a disturbance of the equilibrium of the metal itself. Carbon dioxide is not essential for corrosion; it plays a secondary part only. Nor are the formation and effect of hydrogen peroxide (Traube, A., 1885, 1105) confirmed. In presence of oxygen, the velocity of corrosion $= K(C_0 - C_1)$, C_0 being the solubility of the oxygen in the electrolyte and C_1 its concentration near the iron. Corrosion is greatest where $C_0 = C_1$, that is, where the metal is in contact both with air and water. In weak salt solutions, no effect is observed. Most electrolytes have a maximum "critical" concentration at which corrosion is greatest, but above this concentration the effect diminishes, and many solutions

have also a "limiting" concentration at which corrosion ceases entirely. Tables are given showing values for various electrolytes. Solutions of sodium carbonate above $\pm 0{\cdot}1N$ strength, and of sodium hydroxide above $0{\cdot}02N$, are rust-preventive. Ammonium salts generally are very corrosive. The potential of the metal is a dominating factor; an *E.M.F.* of 0·793 volt was obtained with pure iron, which was slightly altered by compression or cooling, but slowly regained its original value. Impurities in iron, by setting up local *E.M.F.*'s up to 20—90 millivolts, accelerate corrosion. The effect of other metals depends on their comparative potentials. Contact with copper increased corrosion of iron by 25—47%, and with nickel by 14—19%. No definite data are obtainable with most metals, however. The composition of rust varies considerably. The author gives many references to the work of other investigators. W. J. W.

Constitution of Iron–Chromium Alloys. Ernst Jänecke (*Zeitsch. Elektrochem.*, 1917, **23**, 49—55).—The system iron-chromium has been examined by means of fusion curves and by the microscopic study of polished sections of the various alloys. The fusion curves were made in a dynamidon (alumina and clay) furnace fitted with a magnesite crucible and heated electrically. The temperatures were automatically recorded by means of a thermo-element and recorder. Curves were produced for six alloys lying between the limits 10Fe:90Cr and 90Fe:10Cr, and all indicate that the system iron–chromium consists of a single eutectic which can form mixed crystals with either component. The eutectic contains 75% of chromium and melts at 1320°; the limits over which mixed crystals are formed are 55—85% of chromium. The microscopic investigation shows that the crystalline structure is finer the greater the percentage of chromium. The alloys are all tough, and only in the case of the alloys rich in chromium (above 80%) is it possible to break them on an anvil. The alloys are easily scratched by steel and are easily polished. Nitric acid, even when boiling, is without action, but hot 1:1 sulphuric acid attacks them readily. The present results are at variance with previously published results of Treitschke and Tammann (A., 1907, ii, 958), who regard the system as pseudobinary with a single compound of undetermined composition. The author attributes Treitschke and Tammann's results to the presence of aluminium in the chromium used by them. J. F. S.

Chromium Azoimide. E. Oliveri-Mandalà (*Gazzetta*, 1919, **49**, ii, 43—46. Compare Curtius and Rissom, A., 1899, ii, 90).—Chromium azoimide may be separated by means of the insoluble *pyridine* compound, $Cr(N_3)_3,3C_5H_5N$, which forms green, crystalline crusts and explodes violently when heated. When boiled, its concentrated aqueous solution deposits mixtures of basic salts of various compositions, the *basic azoimide*, $OH{\cdot}Cr(N_3)_2,2H_2O$, which is far less explosive than the original compound, being isolated. Aqueous solutions containing chromium azoimide exhibit the green colour

peculiar to complex chromium salts, and do not yield a precipitate with ammonia solution; even when the experimental conditions are widely varied, addition of silver nitrate does not cause precipitation of the whole of the nitrogen as silver azoimide. T. H. P.

The Crystallography of Uranyl Nitrate Hexahydrate. E. QUERCIGH (*Riv. min. crist. Ital.*, 1915, **44**, 6—14).—A detailed description is given of the crystals, which varied widely in habit according to the solvent employed in their formation.

CHEMICAL ABSTRACTS.

New Method of Analysis of Platinum Ores and Compositions of Native Platinums from the Urals. LOUIS DUPARC (*Helv. Chim. Acta*, 1919, **2**, 324—337).—The modes of occurrence and processes of extraction of platinum in the Urals, and a new method for analysing platinum ores, are described; a table is also given showing the mean compositions of samples of platinum from the chief centres in the Urals. [See, further, *J. Soc. Chem. Ind.*, 1919, 822A.] T. H. P.

Mineralogical Chemistry.

Oceanic Salt Deposits. WILHELM GRÜNEWALD (*Inaug.-Diss. Erlangen*, 1913, 44 pp.; from *Jahrb. Min.*, 1916, ii, Ref. 255).—The work is a continuation of that of van't Hoff and Meyerhoffer, and deals mainly with accurate determinations of the solubility relations of the various salts found in the salt deposits; 1000 mols. H_2O at 25° dissolve 88 mols. KCl, or 111 mols. NaCl, or 12 mols. K_2SO_4; at 83°, 118 mols. NaCl. Magnesium sulphate heptahydrate at 25°, 1000 mols. H_2O contain 55 mols. $MgSO_4$. Potassium chloride and carnallite at 25°, 1000 mols. H_2O contain 72·5 mols. $MgCl_2$ and 11 mols. KCl. Magnesium sulphate heptahydrate and picromerite (schœnite) at 25°, 1000 mols. water contain 58·5 mols. $MgSO_4$ and 5·5 mols. K_2SO_4. Potassium sulphate and picromerite at 25°, 1000 mols. H_2O contain 22 mols. $MgSO_4$ and 16 mols. K_2SO_4. Sodium chloride and magnesium chloride hexahydrate at 25°, 1000 mols. H_2O contain 103 mols. $MgCl_2$ and 2·5 mols. NaCl. L. J. S.

An Unlisted Mineral. GEORGE J. HOUGH (*Amer. J. Sci.*, 1919, [iv], **48**, 206).—A new silver–copper mineral, found in a pocket at a depth of 1100 feet in the Cocinera Mine at Ramos, in San Luis Potosi, Mexico, is described. The mineral is silver-grey in colour with a metallic lustre and slowly tarnishes to black; its streak is leaden-grey, and hardness 2·5. It has D 6·14, and is quite homogeneous. Its composition is: copper, 60·58%; silver, 27·54%; iron, 1·55%; and sulphur, 9·65%, which would give as the empirical

formula $AgCu_4S$. The author suggests the name *cocinerite* for the mineral. J. F. S.

Exchange of the Bases of Zeolites in Neutral Salt Solutions. Ilse Zoch (*Chemie der Erde*, 1915, **1**, 55 pp., and *Inaug.-Diss., Berlin*; from *Jahrb. Min.*, 1916, ii, Ref. 266—267).—Various zeolites were shaken in solutions of ammonium chloride. Although the reaction proceeds at first with comparative rapidity, yet equilibrium is only slowly reached. For example, for stilbite in grains of 0·25—0·5 mm. equilibrium is reached after forty to fifty days. Temperature, fineness and quantity of powder, and strength of the solution, all exert an influence. There is an exchange only of the bases, calcium, sodium, and potassium, these being replaced by an equivalent amount of ammonium; alumina and silica do not pass into solution, and the amount of chlorine in the latter remains constant. The substitution is accompanied with a change in the optical characters of the material. Chabazite is most readily acted on, then stilbite, heulandite, and harmotome in the order named, whilst scolezite is scarcely affected. Silver nitrate solution acts readily on stilbite at 50°. Copper chloride solution acts on chabazite, stilbite, and heulandite as shown by a change in the birefringence and the green staining; the latter is removed again when the copper is replaced by ammonium.

L. J. S.

Analytical Chemistry.

New Method of Chemical Analysis. A. W. Hull (*J. Amer. Chem. Soc.*, 1919, **41**, 1168—1175).—A method of analysis based on the use of *X*-rays is described. The method consists in passing a beam of monochromatic *X*-rays through the powdered material contained in a glass tube and photographing the diffraction pattern produced. The apparatus required consists of a Coolridge *X*-ray tube fed by a transformer; in front of the tube a screen of suitable metal is placed which acts as a filter (for a molybdenum tube, a zirconium filter is used). The rays passing through the filter are cut down to a narrow beam by means of two lead slits; this beam then passes through the material under analysis, and a fraction of it is scattered. The material is placed at the centre of a photographic film which is bent over a semi-circular strip of wood or brass. After exposure for an hour the film is developed and the photograph compared with photographs prepared from known substances. Substances with a similar crystal structure yield similar patterns, but the intensity and spacing of the individual bands varies with each substance. Examples are given showing that this method is capable of use for analysing mixtures and also gives an approximate quantitative analysis of simple mixtures. J. F. S.

Electrical Apparatus for Use in Electrometric Titrations. Howard S. Roberts (*J. Amer. Chem. Soc.*, 1919, **41**, 1358—1362).—A potentiometer is described for use in electrometric titrations. This instrument does not necessarily give the *E.M.F.* readings in volts, but in arbitrary units, since all that is desired in this type of work is the inflexion point of the *E.M.F.* The instrument consists of a rheostat on which two sliding contacts work. The contacts indicate on scales which are numbered in opposite directions, the one from 0 to 100 and the other from 100 to 200. Thus when the point 100 represents zero potential, readings may be made with a solution which changes the sign of its *E.M.F.* without the use of reversing keys and without introducing a minus sign into the figures. The potentiometer is used with a single dry cell and a high resistance galvanometer. J. F. S.

Anti-reflux Device Applicable to Evolution Methods of Analysis. P. L. Robinson (*Chem. News*, 1919, **119**, 159—161).—The apparatus consists of a liquid trap placed between the reaction flask and the absorption vessel; air is admitted through a vertical tube extending into the liquid, when the pressure in the reaction flask diminishes. A similar apparatus for use in the estimation of sulphur in steel is described. W. P. S.

Colorimetric Scale for the Rapid Estimation of the Free Hydrochloric Acid in Liquids by means of a Solution of Brilliant-green. Maurice Delort and Roche (*Compt. rend. Soc. Biol.*, 1918, **81**, 646—649).—Two c.c. of a solution (1:5000) of brilliant-green (tetraethyldiaminotriphenylcarbinyl sulphate) are mixed with 2 c.c. of the liquid under examination, for example, gastric juice, and the free hydrochloric acid is estimated by comparison with a colorimetric scale. The colour changes are, to green (0·005% hydrochloric acid), then to yellowish-green (0·03% hydrochloric acid), and then to a more pronounced yellow tint (0·2% hydrochloric acid). Decolorisation occurs in one to two hours with a 0·1% solution of hydrochloric acid, but no decolorisation occurs with acid at a concentration less than 0·03%. The colorimetric scale is furnished by mixing an unfiltered, aqueous alcoholic solution of methylene-blue (1:100), a filtered, neutral solution of potassium chromate (1:20), an unfiltered, aqueous alcoholic solution of eosin (0·10:100), and water in such proportions as to yield mixtures exhibiting tints corresponding with those produced by 0·025%, 0·05%, 0·075%, 0·10%, 0·15%, and 0·2% solutions of free hydrochloric acid; the mixtures are kept in small, sealed tubes. A solution of brilliant-green in distilled water is used as a control. A solution of brilliant-green becomes more or less turbid when it is mixed with undistilled water. Attempts to reproduce the turbidity in the colorimetric scale by means of soap, tincture of gum benzoin, etc., did not give satisfactory results; there is, however, little difficulty in such cases in comparing the opaque tints with the transparent tints of the colorimetric scale. The comparison of tints should be made rapidly (especially for hydrochloric acid at the

higher concentrations) before decolorisation occurs; comparison is made in diffused light and the tubes of the colorimetric scale should be kept in the dark when not in use. The presence of lactic acid causes little difficulty since the tint which it produces differs (in being nearly turquoise blue) from that due to hydrochloric acid and is much less intense than the latter. The influence of combined hydrochloric acid on the reaction is also practically negligible. This is shown by the concordance between estimations of free hydrochloric acid (in presence of combined hydrochloric acid) by this method and by use of Linossier's reagent and by the fact that a hyperacid gastric juice (after exact neutralisation of free hydrochloric acid) gave only a slight colour change when treated with brilliant-green solution, this change in colour being less intense than that corresponding with the minimum of the scale. This method is especially adapted to use under conditions where the usual laboratory facilities are not available.

CHEMICAL ABSTRACTS.

Estimation of Iodides. PAUL GODFRIN (*Bull. Soc. pharm., Bordeaux*, 1919, 16; from *Ann. Chim. anal.*, 1919, [ii], **1**, 295—297).—The method depends on the decomposition of the iodide by potassium dichromate in acid solution, the liberated iodine being titrated with thiosulphate solution. Ten c.c. of a 1% solution of the iodide are treated with 1 c.c. of 10% potassium dichromate solution and 15 drops of hydrochloric acid; 20 c.c. of 10% sodium acetate solution, 50 c.c. of water, and 2 c.c. of starch solution are then added, and the iodine titrated with standardised thiosulphate solution. The method may be applied to the estimation of iodides in urine; the influence of substances which absorb iodine is removed by titrating the sample with iodine before the dichromate is added; the liberation of the iodine in this case is at a maximum in three minutes, and the loss is about 2·5% of the quantity of iodine present. W. P. S.

Estimation of Iodide, Bromide, and Chloride in Presence of Each Other. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1298—1300).—The total halogen content in a mixture of chloride, bromide, and iodide is determined by precipitation with silver nitrate. Iodide alone is determined by the addition of excess of iodate after acidifying with benzoic acid, and titration of the iodine liberated by means of thiosulphate. Iodide and bromide are estimated as follows: 25 c.c. of $N/10$-solution of potassium iodate, 5 c.c. of N-sulphuric acid, and 20 c.c. of water are added to the solution, and the halogen liberated is driven off by boiling in a Kjeldahl flask. Potassium iodide is now added and a few c.c. of sulphuric acid. The iodine liberated is titrated with thiosulphate. The chloride present is then determined by difference. W. S. M.

Detection of the Halogens in Mixtures of their Salts. A. J. JONES (*Chem. and Drug.*, 1919, **91**, 52—53).—Traces of iodide in a bromide or chloride may be detected by the nitrite-

chloroform test, using acetic acid in the proportion of 1 c.c. to 1 gram of the salt and 10 c.c. of water. To detect traces of bromide in chloride or iodide, the salt solution is boiled with the addition of a small quantity of potassium permanganate and phosphoric acid, and the vapours brought into contact with fluorescein paper, the appearance of a red coloration on the paper denoting the presence of bromine. Traces of chloride in iodide or bromide may be detected by treating the salt with chloroform and a mixture of permanganate and phosphoric acid until all the iodine or bromine has been liberated and removed by the chloroform. The aqueous solution is then decolorised with sulphurous acid, the chloride precipitated as silver chloride, and the latter identified by its complete solubility in ammoniacal silver nitrate solution. [See, further, *J. Soc. Chem. Ind.*, 1919, November.] W. P. S.

Iodometric Estimation of Sulphurous Acid and Sulphites. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 1366—1373).—The accuracy of the iodine method of estimating sulphurous acid has been the subject of much investigation, and there is considerable divergence in the literature on the subject. The author prepared a pure solution of sulphur dioxide, free from sulphate, by washing the gas obtained from copper and sulphuric acid with barium nitrate solution, and dissolving it in air-free water containing 5% of ethyl alcohol, the solution being made $N/20$. When sulphurous acid was added to $N/10$-iodine, and the excess of the latter titrated with sodium thiosulphate, very accurate results were obtained. Titration of the iodine by sulphurous acid from a burette until complete reduction took place was also satisfactory. Addition of sodium carbonate or hydrochloric acid introduced errors of 1·2 to 2·6%, due to oxidation by the air. Inaccurate results are obtained if the iodine is added from a burette to the sulphurous acid, and no improvement is gained by adding mannitol (Ruff and Jeroch, A., 1905, ii, 200), sucrose, or alcohol. Solution of pure sodium sulphite, when added to the iodine, gave accurate results, but errors up to 2·8% arose when the iodine was added to the sulphite solution. Addition of potassium iodide, which acts as a catalyst in oxidation, caused errors up to 3·4%, and with sodium hydrogen carbonate divergencies up to 4% were obtained. The author states that inaccuracies are due to oxidation by the air, and denies the influence or formation of free sulphur in the reaction (Volhard, A., 1888, 192). W. J. W.

Estimation of Sulphates in a Concentrated Electrolyte and the Estimation of Sulphur in Foods. VERNON K. KRIEBLE and AUTREY W. MAGNUM (*J. Amer. Chem. Soc.*, 1919, **41**, 1317—1328).—The authors have investigated the sodium peroxide method of estimating sulphur in foods with the double object of preventing firing or explosions during the oxidation and of precipitating completely barium sulphate from the solutions, obtained from the fused material, which have a high concentration

of electrolytes. As the result of a large number of experiments carried out under various conditions, the following method of procedure is recommended: a suitable quantity (2—3 grams) of the material is placed in a nickel crucible of 100 c.c. capacity, mixed with 2—3 c.c. of water, and well stirred with a nickel rod, 5 grams of sodium carbonate are added and well mixed, and then sodium peroxide in small quantities until the whole mass becomes dry and granular. The crucible and contents are carefully heated with a Barthel alcohol lamp until the mixture becomes a brown, homogeneous, fused mass; the mixture is cooled somewhat, and more sodium peroxide added to make a total of 25—26 grams; 3 grams of sodium carbonate are also added and mixed with the peroxide. The crucible is then heated by pointing the flame at a position opposite the level of the contents of the crucible until the first signs of oxidation appear, when the flame is removed and the lid placed in position. After the oxidation is complete, the crucible is heated for a further ten minutes. When the crucible is cool it is placed in 100 c.c. of water and heated until the contents are dissolved, 50 c.c. of concentrated hydrochloric acid are added, and the volume increased to 350 c.c. by the addition of water. The solution is raised to the boiling point and precipitation made with 10 c.c. of 10% barium chloride solution, added by means of a dropper at the rate of 10 c.c. in four minutes. The liquid is kept for forty-eight hours, and then evaporated to dryness, the residue is treated with water, and, after keeping for eighteen hours, the precipitate is collected on a Gooch filter. The results of this method are always high, due to adsorbed material in the precipitate, and should be corrected by an amount which is determined experimentally. The correction is obtained by repeating the estimation with a solution of a known amount of potassium sulphate and finding the amount by which the weight of barium sulphate differs from the theoretical quantity. The difference gives the correction value. J. F. S.

Acidimetric Estimations in Liquids from Aluminium Sulphate Manufacture. I. Bellucci and F. Lucchesi (*Gazzetta*, 1919, **49**, i, 216—241).—The various methods of estimating free and combined sulphuric acid in acid solutions of aluminium sulphate are discussed. T. H. P.

Alkalimetric Titrations in Presence of Alumina. I. Bellucci and F. Lucchesi (*Annali chim. Appl.*, 1919, **11**, 199—204).—The literature of the subject is discussed and criticised (see preceding abstract). T. H. P.

The Micro-estimation of Nitrogen by Direct Nesslerisation, and of Total Solids, in Drop Quantities of Human Blood. Amos W. Peters (*J. Biol. Chem.* 1919, **39**, 285—298).—The estimation of total solids is made by evaporating the known weight of blood, previously diluted with 0·5% sodium fluoride solution, on a weighed quantity of pure talc powder at 75°.

The method of carrying out the digestion of the blood in the micro-Kjeldahl process is minutely described, the most important point in the management of the digestion relating to the process of heating. The colour comparison in the subsequent nesslerisation is made against a single fixed colour standard prepared from picric acid and ferric ammonium sulphate. The conditions of accuracy have been tested, and the method is regarded as trustworthy. J. C. D.

Estimation of Ammonia in Blood. Otto Folin (*J. Biol. Chem.*, 1919, **39**, 259—260).—It is pointed out that the method employed by Morgulis and Jahr (this vol., ii, 371) yields unsatisfactory results unless every reagent used, including the permutite, is absolutely free from ammonia. A method is given for rendering preparations of metaphosphoric acid free from ammonia. When the purified reagents are employed, the amount of ammonia obtained from protein-free blood filtrates is practically nothing, only a greenish-yellow colour being obtained with Nessler's reagent. J. C. D.

Volumetric Estimation of Hydroxylamine. William C. Bray, Miriam E. Simpson, and Anna A. MacKenzie (*J. Amer. Chem. Soc.*, 1919, **41**, 1363—1378).—The authors have investigated three methods for the volumetric estimation of hydroxylamine: (1) the reduction of hydroxylamine to an ammonium salt by an excess of a titanous salt in acid solution, (2) the oxidation of hydroxylamine to nitrous oxide by an excess of ferric sulphate in sulphuric acid solution with titration of the ferrous salt produced, by potassium permanganate solution, and (3) the oxidation of hydroxylamine to nitrous oxide by iodine in a solution kept neutral by means of disodium hydrogen phosphate. The first two methods are found to be accurate, but the iodine method is unsatisfactory. In addition to the known positive error in the ferric salt method, which is due to the addition of permanganate while some hydroxylamine or an intermediate product, nitroxyl, is still present, a negative error due to oxygen of the air is found under certain conditions. Both errors are easily avoided, the latter by adding the hydroxylamine slowly to a boiling solution of ferric sulphate. Three sources of error are met with in the iodine method: (1) that due to incomplete reaction, which may be avoided by the addition of disodium hydrogen phosphate, (2) nitrite formation, which occurs under all the conditions investigated and constitutes a positive error, and (3) absorption of oxygen from the air, which constitutes a negative error. An empirical method is described whereby theoretical results can be obtained by the iodine method, but this is shown to be due to a compensation of the last-named two errors. Hydroxylamine is oxidised mainly to nitrate by an excess of hypochlorous acid. Sodium thiosulphate in a solution of disodium hydrogen phosphate can be quantitatively oxidised to sulphate by iodine. The reaction is rapid at 70°. J. F. S.

Influence of Fluorides on the Oxidimetric Estimation of Nitrous Acid. I. Bellucci (*Gazzetta*, 1919, **49**, i, 209—216).—Lunge's method of estimating nitrous acid by means of permanganate leads to fallacious results if the solution contains also fluorine ions in high concentration. This anomaly is due to the same cause as that observed by Müller and Koppe (A., 1910, ii, 957) in the oxidimetric estimation, also in presence of fluorides, of manganese by Volhard's method, namely, the formation of derivatives of tervalent manganese. In the case of nitrous acid, this inconvenience may be overcome by treating the nitrous acid, in a solution acidified with sulphuric acid, with excess of standard permanganate solution, then adding, after a couple of minutes, potassium iodide solution and estimating the iodine liberated by the excess of permanganate by titration with thiosulphate solution. A blank estimation should also be carried out with the same volume of permanganate as is used to oxidise the nitrous acid.

The case studied by Müller and Koppe is not amenable to this procedure, since addition of the alkaline iodide would there result in liberation of iodine in amount corresponding with the quantity of permanganate initially taken. T. H. P.

Estimation of Citrate-soluble Phosphoric Acid by Petermann's Method. H. Neubauer and E. Wolferts (*Landw. Versuchs-Stat.*, 1916, **89**, 197—202).—New methods are described for preparing Petermann's ammoniacal citrate solution and for applying it to the estimation of the citrate-soluble phosphoric acid of dicalcium phosphate ("Methodes suivies dans l'analyse des matières fertilisantes," Gembloux, 1897). [See *J. Soc. Chem. Ind.*, 1919, 837A.] T. H. P.

Electrolytic Resistance Method of Estimating Carbon in Steel. J. R. Cain and L. G. Maxwell (*J. Ind. Eng. Chem.*, 1919, **11**, 852—860).—A rapid method of estimating carbon in steel has been based on the absorption of the carbon dioxide, obtained by direct combustion, in barium hydroxide solution, and measuring the change in the electrolytic resistance of the solution caused by the precipitation of the barium ions. A simple form of absorption apparatus has been devised for this purpose, containing a cell in which the electrodes can be adjusted so as to give a definite cell constant, and Weibel's galvanometer has been found an accurate instrument for measuring the resistance. The combustion is carried out in an electric furnace, and the carbon dioxide is expelled by a current of air (freed from carbon dioxide). A table showing the percentages of carbon corresponding with the resistance and the temperature of barium hydroxide solutions of definite concentrations has been made, and from this a nomographic chart has been constructed whereby the percentages may be read directly with an error of less than 0·005% of carbon. [See further, *J. Soc. Chem. Ind.*, 1919, 773A.] C. A. M.

Detection of Carbon Monoxide in Air. Desgrez and Labat (*Acad. med.*, 1919; from *Ann. Chim. anal.*, 1919, [ii], **1**, 294—295).—Strips of filter paper are immersed in 10% palladium

chloride solution and then dried in the dark. If a strip, moistened at one end, is suspended in air containing carbon monoxide, the moistened portion becomes grey, brown, or black within six minutes, whilst the dry portion retains its yellow colour. The depth of the coloration depends on the amount of carbon monoxide present; 1 part in 1300 parts of air yields a distinct grey coloration. If the air also contains hydrogen sulphide, the strip should be suspended in a bottle through which the air, previously passed over lead acetate, is aspirated. W. P. S.

Estimation of the Reaction of Natural Waters. J. Tillmans (*Zeitsch. Nahr. Genussm.*, 1919, **38**, 1—16).—The reaction (hydrogen ion concentration) of most natural waters is due to free carbon dioxide and to carbon dioxide combined as hydrogen carbonates, and is conveniently expressed as ten thousandths of a mg. per litre ($=h^*$). In neutral waters $h^*=1$; all values above 1 indicate an acid reaction and all values under 1 an alkaline reaction. Generally, h^* can be calculated with sufficient accuracy by multiplying the mg. of free carbon dioxide per litre by 3 and dividing the result by the number of mg. of carbon dioxide present as hydrogen carbonate per litre of water. The exceptions to this rule are described. In the case of alkaline waters, the alkalinity may be expressed as the reciprocal of h^*. [See, further, *J. Soc. Chem. Ind.*, 1919, November.] W. P. S.

Acidosis. XVI. Estimations of Bicarbonate in the Blood Plasma of Different Species by the Titration and Carbon Dioxide Capacity Methods. Edgar Stillman (*J. Biol. Chem.*, 1919, **39**, 261—265).—The methods employed were those described by van Slyke, Stillman, and Cullen (A., 1917, i, 521; this vol., ii, 298), and examinations of plasma from the blood of man, dogs, sheep, rabbits, and chickens were carried out. Results obtained by titration agreed with those by the carbon dioxide capacity method, as a rule, within less than two millimolecular in plasma bicarbonate concentration. The results confirm the conclusion reached in the former paper that the two methods may be used interchangeably for clinical and for many experimental purposes. J. C. D.

The Estimation of Calcium and Magnesium in Different Saline Solutions. E. Canals (*Bull. Soc. Chim.*, 1919, [iv], **25**, 90—94).—Experiments in which magnesium ammonium phosphate was precipitated by adding a solution of magnesium sulphate to an ammoniacal solution of sodium phosphate containing ammonium chloride showed that considerable excess of phosphate, ammonia, or ammonium chloride or of all three together may be used without the accuracy of the magnesium estimation being thereby affected. Only in special circumstances can magnesium be estimated as oxide or sulphate. Both these compounds are very hygroscopic, and magnesium sulphate is subject to decomposition at a bright red heat. E. H. R.

Separation and Estimation of Magnesium in the Presence of Fixed Alkalis. P. NICOLARDOT and F. DANDURAND (*Rev. Met.*, 1919, **16**, 193—199).—The most trustworthy method for the separation of magnesium from alkalis consists of precipitating the magnesium by means of ammonium phosphate; the details of this method are too well known to need description. A large excess of ammonium phosphate should be avoided; the small excess which is necessary may be removed subsequently by treatment with ferric chloride and ammonia, and the alkalis may then be estimated. Separation of the magnesium by means of ammonium carbonate in alcoholic solution, barium hydroxide, calcium hydroxide, ammonium oxalate, or mercuric oxide is untrustworthy. A simple method for the estimation of magnesium when alkalis are not present (for example, in the analysis of metallic magnesium and its alloys) depends on the precipitation of the magnesium as magnesium fluoride–hydrofluoride; the magnesium chloride, in neutral solution, is treated with a slight excess of ammonium fluoride, the mixture is evaporated to a syrup on a water-bath, and the residue ignited. The ignited residue consists of magnesium fluoride. This method cannot be employed when alkali chlorides are present in the solution. W. P. S.

Estimation of Metallic Zinc Content of Zinc Dust. W. F. EDWARDS (*Chem. and Met. Eng.*, 1919, **21**, 192).—Neither the hydrogen-gas method nor the reduction of potassium iodate is on the whole suited to the evaluation of zinc dust, used or unused, in sherardising. The amalgam method is not satisfactory for practical purposes, even if carried out with careful attention to details in parallel estimations under identical conditions. The reduction of ferric sulphate gives inconsistent results, but with crystallised ferric ammonium sulphate satisfactory results are obtained, the time required being approximately fifteen minutes against six to thirty-six hours for the gas method. The method is as follows: 1 gram of zinc dust is put into a 600 c.c. Erlenmeyer flask, together with 50 grams of ferric alum in crystals and 100 c.c. of water, the whole being constantly stirred. As soon as the zinc dust is dissolved, 100 c.c. of 1:10 sulphuric acid are added, and the solution titrated against potassium permanganate. Comparisons of results obtained on new and used zinc dust by the hydrogen-gas method and the ferric alum method are given, and show good agreement. T. H. B.

Simple Method of Analysing Bearing Metal and Similar Alloys. G. OESTERHELD and P. HONEGGER (*Helv. Chim. Acta*, 1919, **2**, 398—416).—The principles on which the method described is based are as follows. The alloy is dissolved in boiling concentrated sulphuric acid, dissolution being complete in a few minutes even with an alloy rich in lead. The antimony passes quantitatively into solution in the tervalent form and the tin as stannic sulphate. The copper and lead are converted entirely into copper and lead sulphates, subsequent dilution with water resulting in the separa-

tion of crystalline lead sulphate, which is readily removed by filtration through a Gooch crucible. In the filtrate the antimony is titrated directly with potassium bromate, the titrated solution being then reduced and the tin, and afterwards the copper, estimated volumetrically. In presence of tin, antimony, and lead, copper may be estimated in a few minutes by a simplified form of electrometric titration with sodium thiosulphate. [See *J. Soc. Chem. Ind.*, 1919, 824A.] T. H. P.

Estimation of Small Quantities of Mercury in Toxicological Investigations. F. Carrescia (*Boll. chim. farm.* 1919, **58**, 242—244).—Descriptions are given of the methods applied to the estimation of mercury in two cases of attempted poisoning by addition of mercuric chloride to coffee and to a bronchial remedy. [See *J. Soc. Chem. Ind.*, 1919, November.] T. H. P.

A Sensitive Reaction for Manganous Salts. D. H. Wester (*Pharm. Weekblad*, 1919, **56**, 1289—1290).—The author points out that the potassium oxalate test for manganese salts is less sensitive than the tests with lead peroxide and nitric acid, and with persulphate and silver nitrate, both of which are applicable in presence of considerable quantities of chlorides. The reaction may, however, be used as a sensitive test for oxalate. W. S. M.

Estimation of Manganese in Steel by means of Persulphate in the Presence of Chromium and Tungsten. P. Nicolardot and A. Levi (*Rev. Met.*, 1919, **16**, 201—216).—Investigation of the persulphate method showed that the most trustworthy results are obtained under the following conditions. A quantity of 0·2 gram of the steel is dissolved in 10 c.c. of 33% sulphuric acid and 0·5 c.c. of nitric acid; the solution is then cooled, 5 c.c. of saturated silver sulphate solution and 0·5 gram of persulphate are added, the solution is diluted to 50 c.c., heated for three to five minutes in a water-bath, the heating being discontinued when the red coloration appears. The mixture is set aside until cold and then titrated with arsenious acid solution; the latter should contain 0·5 gram of arsenious acid and 2·5 grams of sodium hydrogen carbonate per litre, and be standardised against a steel containing a known amount of manganese. If the titrated mixture is again heated, the manganese is reoxidised (a sufficient quantity of persulphate still remains for this purpose), and the titration may be repeated. If the steel contains a large quantity of chromium and less than 1% of manganese, the amount of the latter should be brought up to about 1% by the addition of manganese, in the form of a standard permanganate solution, after the treatment with persulphate. The following method is recommended in the case of a steel containing chromium, tungsten, and vanadium. A weighed amount of 0·2 gram of the steel is boiled with 25% sulphuric acid and 0·5 c.c. of nitric acid until a precipitate of yellow tungstic acid forms and all black particles disappear; the mixture is cooled, sodium hydroxide is added in quantity sufficient

to dissolve the tungstic acid and precipitate the iron, 3 c.c. of phosphoric acid solution (containing 38% P_2O_5) are added, the mixture again cooled, and slightly acidified with sulphuric acid. If the solution thus obtained is not perfectly clear, the estimation must be recommenced. The solution is then treated with 10 c.c. of saturated silver sulphate solution and 1 to 3 grams of persulphate, heated on a water-bath for three to five minutes, cooled, 0·002 gram of manganese (in the form of potassium permanganate solution) is added, and the solution is titrated with arsenious acid solution. The quantity of manganese added is deducted from the result obtained. The authors do not think it advisable to attempt to estimate the chromium and the manganese in the same portion of the sample. W. P. S.

Estimation of Iron in Iron Ores by means of Permanganate. R. Schwarz (*Chem. Zeit.*, 1919, **43**, 499—500).—A reply to Brandt (this vol., ii, 373).—The author maintains that the use of sodium silicate in the titration is trustworthy under the conditions described by himself and Rolfes (this vol., ii, 170). W. P. S.

Electrometric Titrations, with Special Reference to the Estimation of Ferrous and Ferric Iron. J. C. Hostetter and H. S. Roberts (*J. Amer. Chem. Soc.*, 1919, **41**, 1337—1357).—Experiments are described on the estimation of ferrous iron by titration with potassium dichromate and potassium permanganate in which the end-point of the reaction is obtained from the *E.M.F.* of the solution against a calomel electrode. The work is extended to the estimation of ferric iron by means of stannous chloride and the titration of potassium dichromate with stannous chloride. The electrical apparatus used in the work is that described by Roberts (see this vol., ii, 471). A special "titration head" is used to cover the flasks in which the titration is carried out. This consists of a glass cap with three openings at the top; through the first opening a glass tube from the calomel electrode enters, the second opening admits the tip of the burette, and the third carries a platinised platinum electrode and admits a current of carbon dioxide. Using this method, solutions of potassium dichromate as dilute as 0·0005*N* may be employed. The electrometric method makes it unnecessary to remove the excess of a reducing agent which has been added in the reduction of a ferric salt. Conditions, such as acidity, need not be controlled except within very wide limits, and hydrochloric, sulphuric, or hydrofluoric acid may be used. The sensitiveness and accuracy of the method make possible the estimation of a few tenths of a milligram of tin, chromium, ferrous, or ferric iron in the presence of large quantities of some other elements, and its use in the blank estimations involved in some of the ordinary estimations by reducing or oxidising agents. The time within which an estimation can be carried out is greatly shortened. The content of ferrous and ferric iron in a silicate, for example, can be deter-

mined in from fifteen to thirty minutes. The precision attainable is comparable to the best of the ordinary volumetric methods.

J. F. S.

New Method for the Estimation of Chromium. A. Terni and P. Malaguti (*Gazzetta*, 1919, **49**, i, 251—256).—The method previously given for the detection of chromium (A., 1913, ii, 881) is applicable to the estimation of this metal, the procedure being as follows. The solution of the chromic salt is boiled with 20 c.c. of nitric acid (D 1·4) and about 1 gram of lead dioxide in a covered 200 c.c. beaker until the volume is reduced to a few c.c. The liquid is then diluted with 40—50 c.c. of water, treated with sufficient 25—30% sodium hydroxide solution to redissolve the precipitated lead chromate, heated to incipient boiling, and filtered into a conical litre flask, the residue on the filter being washed five or six times with boiling water rendered slightly alkaline with sodium hydroxide. The filtrate is diluted to 150—200 c.c., sufficient nitric acid (D 1·2) absolutely free from nitrous acid being added to dissolve the lead chromate almost completely, and then a further 25 c.c. of the same acid. The acid liquid is treated with 5—10 c.c. of 10% potassium iodide solution, and the iodide liberated titrated with sodium thiosulphate solution containing about 25 grams per litre, previously standardised, in presence of 25 c.c. of the nitric acid of D 1·2, by means of *N*/10-potassium dichromate solution. The method gives good results and is not invalidated by the presence of iron, manganese, or aluminium.

T. H. P.

Rapid Method of Estimating Uranium in Carnotite. C. E. Scholl (*J. Ind. Eng. Chem.*, 1919, **11**, 842).—The difficulties of separating uranium in the presence of iron, aluminium, and vanadium, which are the principal impurities in carnotite, are obviated by adding an excess of ferric iron to the solution, precipitating the iron, vanadium, and most of the aluminium with sodium carbonate at about 90°, and then precipitating the uranium from the boiling filtrate by means of sodium hydroxide. The precipitate is dissolved in dilute nitric acid, the uranium again precipitated by means of ammonia at 90°, and the precipitate ignited and weighed as uranium oxide, U_3O_8. [See, further, *J. Soc. Chem. Ind.*, 1919, 778A.]

C. A. M.

Rapid Method for the Estimation of Titanium in Titaniferous Iron Ores. John Waddell (*Analyst*, 1919, **44**, 307—309).—The ore is fused with sodium peroxide in an iron crucible, the mass dissolved in water and sulphuric acid, tartaric acid is added, and the iron precipitated as sulphide by means of hydrogen sulphide and ammonia. After removal of the iron sulphide, the solution is boiled with the addition of sulphuric acid to expel hydrogen sulphide, and the titanium then precipitated by means of "cupferron" (the ammonium salt of nitrosophenylhydroxylamine), or the titanium may be estimated colorimetrically by

hydrogen peroxide. [See, further, *J. Soc. Chem. Ind.*, 1919, 775A.] W. P. S.

Estimation of Zirconium as Phosphate. P. NICOLARDOT and A. RÉGLADE (*Ann. Chim. anal.*, 1919, [ii], **1**, 278—281. Compare this vol., ii, 180).—Zirconium may be precipitated quantitatively from a 10% sulphuric acid solution by means of ammonium phosphate; two hours should elapse before the precipitate is collected. Aluminium, iron, chromium, and nickel do not interfere, but the iron should be reduced to the ferrous condition before the zirconium is precipitated. Titanium must not be present. Bismuth is precipitated as phosphate from an acid solution, but this metal rarely occurs with zirconium. W. P. S.

Modified Method for the Analysis of Mixtures of Ethylene and Acetylene. WILLIAM H. ROSS and HARLAN L. TRUMBULL (*J. Amer. Chem. Soc.*, 1919, **41**, 1180—1189).—A method of estimating acetylene in mixtures with ethylene and other singly or doubly linked hydrocarbons, based on observations of Chavastelon (A., 1897, i, 545), is described. When acetylene is passed into an excess of a neutral solution of silver nitrate, the solution becomes acid, on account of the reaction $C_2H_2+3AgNO_3=C_2Ag_2,AgNO_3+2HNO_3$. The method described consists in shaking a measured volume of the gaseous mixture with a 5% solution of silver nitrate and determining the acidity by titration with standard sodium hydroxide. The titration is effected as follows: after absorption is completed, sodium hydroxide is added to the solution containing the precipitated silver acetylide until the brown colour of silver oxide appears; the excess of silver is then precipitated with 20% sodium chloride solution, and the excess of free alkali in solution finally estimated by titration with standard hydrochloric acid, using methyl-orange as indicator. The method is rapid, accurate, and simple of manipulation, and has the added advantage of giving accurate results for acetylene in mixtures of ethylene or of a gas of such similar properties as vinyl bromide, which is readily absorbed by bromine, fuming sulphuric acid, and by neutral or ammoniacal silver nitrate. J. F. S.

Analysis of Sulphonyl Chlorides of Aromatic Substances. F. NEITZEL (*Chem. Zeit.*, 1919, **43**, 500).—Three grams of the powdered substance are mixed with 10 c.c. of water, and free sulphonic acids and mineral acids are neutralised with sodium hydroxide solution, using phenolphthalein as indicator; an excess of $N/1$-sodium hydroxide solution and 20 c.c. of alcohol are then added, the mixture is heated under a reflux apparatus for fifteen minutes, and the excess of alkali is titrated. The quantity of alkali used for the hydrolysis is a measure of the amount of sulphonyl chloride present. W. P. S.

Detection of Methyl Alcohol. HANS WOLFF (*Chem. Zeit.*, 1919, **43**, 555).—The presence of higher alcohols in ethyl alcohol

renders the detection of methyl alcohol in the latter untrustworthy if the method used depends on the oxidation of the methyl alcohol and identification of the resulting formaldehyde; the higher alcohols, on oxidation, yield substances which give the same coloration with the morphine–sulphuric acid reagent as does formaldehyde (compare Salkowski, this vol., ii, 249). If, however, *apo*morphine is used in place of morphine in the test, formaldehyde yields a bluish-violet coloration, whilst the oxidation products of the higher alcohols give a yellow or reddish-brown coloration.

W. P. S.

Estimation of Cyanides, Cyanates, and Bromides Present Together. Giuseppe Velardi (*Boll. chim. farm.*, 1919, **58**, 241).—Titration with silver nitrate solution gives, in alkaline solution, the cyanide; in solution neutralised with acetic acid, the bromide, cyanide, and cyanate together; in solution acidified with nitric acid, the cyanide and bromide. [See *J. Soc. Chem. Ind.*, 1919, 815A.]

T. H. P.

A Method of Tissue Analysis: Applied to the Posterior and Anterior Lobes of Cattle Pituitaries. C. G. MacArthur (*J. Amer. Chem. Soc.*, 1919, **41**, 1225—1240).—A modification of Koch's method of tissue analysis is described in which the amount of material required is usually only 10 grams, but may be as low as 2 grams (compare A., 1910, ii, 78—79). The constituents are separated into three groups, proteins, lipins, and extractives, and many instructive determinations made on aliquot parts of each fraction.

The material is first left for several weeks with alcohol, then heated to the boiling point on a few occasions during several days, and finally filtered through a weighed, paper-lined, perforated crucible into a tared beaker, the residue being rinsed with hot alcohol a few times. The residue is next left overnight with ether, warmed several times, and again filtered, using the same crucible and beaker. It is then finely ground and digested with small volumes of hot water, the extract being filtered through the same crucible into a different beaker, evaporated to about 5 c.c., diluted with alcohol, boiled to coagulate the protein, and filtered into the first beaker. All the residues are then transferred by means of alcohol to the crucible, which is placed in a continuous extractor and digested with 95% alcohol for thirty hours, and with chloroform for ten hours. The residual protein is heated in an oven at 105° to constant weight, and the various extracts evaporated in the tared beaker to give the weight of extractives plus lipins. The dried extract is then made into an emulsion with about 40 c.c. of water, treated with 0·5 c.c. of hydrochloric acid to precipitate lipins, centrifuged, and the clear liquid decanted into a 100 c.c. flask containing 5 c.c. of chloroform, shaken, and the aqueous portion poured off into another centrifuge tube, centrifuged, and the clear solution transferred to a second 100 c.c. flask. The lipin residue is treated in the same way with two smaller portions of dilute hydrochloric acid, and finally dissolved in a mixture of alcohol and

chloroform (10:1) in the first 100 c.c. flask, and the volume made up to the mark. The aqueous solution is also made up to 100 c.c.

The further examination of the three fractions follows the usual methods of biochemical analysis, of which the following is a summary. *Extractives.*—(1) Dry weight, ash, and with this any desired inorganic constituents, such as calcium and magnesium. (2) Total nitrogen, by the Kjeldahl method. (3) Nitrogen as ammonia, by rendering a portion slightly alkaline and aspirating the ammonia into 0·01*N*-acid, after which urease is added to the neutralised liquid and nitrogen as urea estimated. (4) Amino-nitrogen, by Van Slyke's micro-method. (5) Creatine and creatinine, by the picric acid, colorimetric method. (6) Uric acid, by the Folin and Denis colorimetric method (A., 1913, ii, 162, 444). (7) Sugar and other substances which reduce Fehling's solution. (8) Total sulphur and sulphur as sulphates. (9) Total phosphorus and phosphorus as phosphates. *Lipins.*—A portion of the solution is evaporated to dryness, hydrolysed by boiling with dilute hydrochloric acid, and thus differentiated into a lipin residue, which is redissolved in chloroform, and a hydrolysis filtrate. Total nitrogen, sulphur, and phosphorus are estimated in the residue, and the filtrate is examined as follows. (1) Total nitrogen. (2) Amino-nitrogen. (3) Volatile amine nitrogen, and, with the same portion, choline nitrogen. (4) Iodine absorbed, by Hübl's method. (5) Total sulphur. (6) Sugar, by the picric acid method. The original lipin solution is also used for the estimation of phosphorus, nitrogen, sulphur, calcium, the iodine value, and also cholesterol, by Bloor's method (A., 1917, ii, 275). *Proteins.*—Phosphorus, sulphur, calcium, chlorine, and total nitrogen are estimated as usual and then the further differentiation is made by Van Slyke's improved method (A., 1915, ii, 851), the nitrogen being recorded as (1) humin nitrogen, (2) ammonia nitrogen, (3) basic nitrogen, (4) arginine nitrogen, (5) histidine nitrogen, (6) lysine nitrogen, (7) cystine nitrogen, (8) mono-amino-nitrogen, (9) non-amino-nitrogen, and (10) α-amino-nitrogen.

The example of the application of this method which is described, is the analysis of the pituitary lobes. The anterior lobe contains 2·4% more solid matter and 4% more protein than the posterior lobe, but there is a great similarity between the proteins of the two lobes. The posterior lobe is 0·9% richer in lipins, these resembling the lipins of the grey matter of the cortex, and also contains 0·9% more extractives, the excess being largely due to non-phosphate phosphorus, amino-nitrogen, and undetermined nitrogen. Both lobes resemble each other so closely that, in spite of their different origin, it may be assumed that they develop together.

J. C. W

General and Physical Chemistry.

Eykman's Refractometric Investigations in Connexion with the Presentation of the Edition of His Works. A. F. Holleman (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1200—1203).—A short account of Eykman's unpublished work on the refractometric measurements of organic compounds given on the occasion of the publication of a collection of his published and unpublished work. J. F. S.

Molecular Refractivity of Cinnamic Acid Derivatives. Eric Walker and Thomas Campbell James (T., 1919, **115**, 1243—1247).

The Line Spectrum of Sodium as Excited by Fluorescence. R. J. Strutt (*Proc. Roy. Soc.*, 1919, [A], **96**, 272—286).—Bakerian Lecture. An improved sodium vapour lamp is described. This consists of a dumbbell-shaped quartz tube placed vertically. In the lower bulb is a pool of sodium which constitutes the cathode. Electric connexion is made by means of an iron or copper wire. The anode consists of a tungsten rod. The lamp is evacuated by means of a Gaede pump. A concentric ring burner surrounds the base of the cathode bulb, by means of which the sodium is kept at a temperature of 180°. The lamp can be run for short periods by a current of 5—6 amps. on a 200 volt circuit, but for prolonged working a lower current, 2·5 amps., is preferable. The lamp is started by means of an induction coil, the terminals of which are connected to the cathode and the constriction of the lamp tube. Using the light from this lamp, the author has examined the resonance effects of sodium vapour. It is shown that excitation of sodium vapour by the second line of the principal series leads to emission of both 3303 and the *D* lines, and that excitation of the *D* lines leads to the emission of the *D* lines only, with 3303. When *D* light falls on sodium vapour of appropriate density, it is known that an intense surface emission occurs from the front layer, and a weak one from succeeding layers. Analysis by absorption in an independent layer of sodium vapour shows that the superficial emission is more absorbable, and therefore nearer the centre of the *D* lines. The breadth of the *D* lines in superficial resonance has been estimated by interferometer methods. It is found to correspond with the breadth conditioned by the Doppler effect, on the assumption that the luminous centre is the sodium atom. Polarisation could not be detected in the ultra-violet radiation, although in accordance with previous observers it was readily observed in *D* resonance. J. F. S.

The Ultimate Rays in the Arc Spectra of the Elements. M. A. CATALÁN (*Anal. Fis. Quim.*, 1917, **15**, 487—498, and 1918, **16**, 513—519).—A criticism of the conclusions of Gramont (A., 1907, ii, 517, and A., 1908, ii, 645) regarding the ultimate rays of a spectrum. Contradicting the assertion of Gramont, the author shows that in general the ultimate rays in the arc spectra are those of the greatest intensity. This conclusion is supported by a special study of the arc- and spark-spectra of columbium, zirconium, and titanium.

W. S. M.

The Logarithmic Law connecting Atomic Number and Frequency Differences in Spectral Series. GLADYS A. ANSLOW (*Physical Rev.*, 1919, **13**, 326—336).—Straight lines are obtained by plotting the logarithms of the atomic numbers against the logarithms of the constant frequency differences occurring in the spectral lines of most of the alternate members of Groups I, II, and III of the periodic table; also for sulphur and selenium. Two systems of four approximately straight lines approaching parallelism result when the family has both doublet and triplet series. Equations derived are of the form $\nu=(N/mnk)^A$, where N is the atomic number, A is a constant depending on the system, n is an integer which is the same for both families in any group, k is a constant, 0·080, and m acquires successive integral values for the ν, $\nu_1+\nu_2$ and ν_1 equations. Elements of high atomic number should lie above the family line. These results indicate the need of modifying the Bohr-Sommerfeld theory of atomic structure before using it for predicting optical series.

CHEMICAL ABSTRACTS.

The Constitution of the Atom and the Properties of Band Spectra. H. DESLANDRES (*Compt. rend.*, 1919, **169**, 745—752).—A continuation of the theoretical discussion of this subject (compare this vol., ii, 206, 310, 441) and its application to the band spectra of carbon, nitrogen, and cyanogen. The following explanation of the known facts is given. The nucleus of the atom is a cylinder with circular base, which rotates round its axis, its thickness in the direction of the axis being the same for all atoms, but the diameter of the circular base being variable. The nucleus is the seat of longitudinal vibrations developed in the direction of the axis. The thickness being constant, the fundamental vibration is the same for all the elements, the higher harmonics giving the frequencies of the band maxima in the successive spectra. On the main longitudinal vibration are superposed the vibrations of the rings of electrons in three directions in space. The divisions imposed on the nucleus by the nodal surfaces may explain the variations of the elementary groups and their simplification with increasing frequency.

These vibrations require that the shocks in the direction of the axis are propagated with a velocity notably inferior to that of light. The special substance of the nucleus is supposed to be electrified in its mass, and can be likened to ordinary matter rather than to a vacuum, for the propagation of small displacements.

W. G.

Study of the Stability of some Solutions of Enzymes and Alkaloids by means of Ultraviolet Absorption Spectra. The Particular Cases of Pancreatin and Morphine. Horacio Damianovich and Adolfo Williams (*Anales Soc. Cient. Argentina*, 1917, **84**, 79—91).—In order to determine the degree of absorption, Dhere's method was used ("Spectrographic Researches on the Absorption of Ultraviolet Rays by Albuminoids, Proteins, and their Derivatives," Univ. of Fribourg, 1909). Aqueous alkaline solutions of pancreatin yielded spectra indicating a gradual absorption in the extreme ultraviolet, but without any band indicating selective absorption. Compared with Dhere's results a notable difference was observed. Albuminoid substances show an absorption band in the ultraviolet spectrum which for a given concentration and thickness includes radiations between 2927 Å. and 2628 Å., whereas in the given case the band did not appear in a solution of 10:1000 strength and 5—10 mm. thickness. Solutions were submitted to temperatures between 40° and 110° for one-half to forty-eight hours. Some alteration in the absorption was noticeable; the conclusion was reached that temperature influences the action. Substances such as glycerol, peptone, and casein, which protect trypsin or pancreatin against the destructive action of heat, act in a similar way towards causing a variation in the ultraviolet spectrum. A solution of morphine (1:10,000) showed appreciable absorption in the ultraviolet, as did also solutions of theobromine, but no band was observed, although neutral aqueous solutions of the hydrochloride showed a faint band between 2950 Å. and 2767 Å. The addition of sodium carbonate (3% solution) to a solution of morphine hydrochloride (1:1000) produced absorption of the extreme ultraviolet and a clear absorption band which increased somewhat with the temperature. Sodium hydroxide causes a similar displacement.

Chemical Abstracts.

Observations and Measurements on Optically Active Crystals ($NaClO_3$). Eligio Perucca (*Nuovo Cim.*, 1919, [vi], **18**, ii, 112—154).—The author describes a new polarimetric arrangement, which he has applied to the measurement of the rotatory power of pure, crystalline sodium chlorate and of crystals of the chlorate coloured with "extra China blue" [probably sodium (or ammonium) triphenyltri-*p*-aminodiphenyltolylcarbinoldi-(or mono-)sulphonate], which exhibits a very sharp absorption band in the green. These coloured crystals are obtained, although not always, by moderately rapid cooling of a hot saturated solution of the chlorate and the colouring matter; ultramicroscopic examination of the crystals shows that the blue dye is not present in them in the colloidal condition.

The results obtained indicate that only as a first approximation can the rotatory power of solid sodium chlorate be regarded as a constant, variations greater than the experimental error being observed with different crystals and also with one and the same crystal in different directions and at different points. The mean value obtained for $[\alpha]_D^{13}$ is $+3{\cdot}120°$. The rotational dispersion,

which shows no deviations from the curve of normal dispersion greater than the errors of observation, may be expressed for the temperature 13° by the following equation, λ being in $\mu\mu$ and $[\alpha]_\lambda$ in degrees: $[\alpha]^\lambda = 1168300/\lambda^2 - 0{\cdot}3514 + 0{\cdot}000000306\,\lambda^2$; Lowry's formula, $[\alpha]_\lambda = a/(\lambda^2 - b)$ (T., 1913, **103**, 1067) is inapplicable in this case.

With the coloured crystals, for the light comprised in the spectral zone absorbed (maximal absorption at about $\lambda = 548\ \mu\mu$), the rotatory power is found to vary when the crystal is rotated round the light ray as axis, that is, to vary with the azimuth of the crystal with respect to the incident luminous vibration. The course of this variation is sinoidal, and for $\lambda = 546{\cdot}1$ the maximum variation amounts to as much as 1° per 3·66° for a thickness of 1 millimetre. With crystals deeply coloured, more marked effects still are observed; thus, in one case, for $\lambda = 589{\cdot}3\ \mu\mu$, the difference between the maximal and minimal rotations per millimetre of thickness reached 1·3°. In no instance, however, was change in the sign of the rotation found. There appears to be no very simple relation between the intensity of the coloration and the extent of the variation in rotation. This phenomenon persists without marked alteration when the crystals are heated to about 85°, but at this temperature it suddenly disappears and does not reappear when the crystals are cooled.

In these artificially coloured sodium chlorate crystals there is, as a rule, co-existence of two tetrahedra, each of which, united to a pentagonal dodecahedron, is characteristic of crystals having rotatory power of a certain sign and of normal magnitude at all points. Groth (*Ann. Phys. Chem.*, 1876, **158**, 214) refers to the possibility of the co-existence of two tetrahedra in a single crystal of sodium chlorate, but the author was unable to obtain such a crystal under widely varying conditions of crystallisation. T. H. P.

Precision Measurements in the *X*-Ray Spectra. II. The *X*-Ray Spectrum of Tungsten. Manne Siegbahn (*Phil. Mag.*, 1919, [vi], **38**, 639—646. Compare this vol., ii, 261).—The *K* and *L* series of *X*-ray lines have been measured for tungsten by means of a spectrograph built on the same principle as that previously described (*loc. cit.*). The measurements were made with rock-salt ($\log 2d = 0{\cdot}7503541$) and calcite ($\log 2d = 0{\cdot}7823347$), and the two sets of results shown to be remarkably close to one another, a fact which speaks for the accuracy of the calcite lattice constant in reference to that of rock-salt. In the *K* series the strongest line, $K\alpha$, has the value $208{\cdot}85\,XU$, the α_2 line is determined with reference to the α_1 line and the value $K\alpha_2 = 213{\cdot}52\,XU$ obtained. The lines $K\beta_1$ and $K\beta_2$ have the values 184·36 and 179·40 respectively. The values are compared with those of de Broglie, Hull and Rice, Dauvillier, and Dershem, and those of the last-named shown to be most nearly in accord with the author's work. The measurement of the *L* series was carried out with the vacuum spectrograph previously described (*loc. cit.*). The following values were obtained: $L\alpha_1$, 1473·48; $L\alpha_2$, 1484·52; $L\beta_1$, 1279·17; $L\beta_2$, 1241·91; and $L\gamma_1$,

1095·53. The fainter lines of this series have been measured with reference to one of the stronger lines, and the following frequency differences obtained: $\epsilon-\eta=l-\eta=98{\cdot}76$; $\beta-\alpha'=\beta_1-\alpha_2=98{\cdot}54$; $\delta-\gamma=\gamma_1-\beta_2=98{\cdot}05$; $\theta-\zeta=\gamma_2-\beta_5=97{\cdot}55$. These figures confirm to a certain extent Sommerfeld's view that the L series can be divided into two groups with constant frequency differences between the lines. J. F. S.

Precision Measurements in X-Ray Spectra. III. An X-Ray Spectrograph for Medium Wave-lengths. Manne Siegbahn and A. B. Leide (*Phil. Mag.*, 1919, [vi], **38**, 647—651. Compare preceding abstract).—An X-ray spectrograph is described which is designed to bridge the regions measured by the instruments described in the previous papers (*loc. cit.*). In the present instrument the slit is placed behind the crystal. The crystal table is in fixed connexion with a high precision circle scale which can be turned in relation to the slit and plate-holder. To fix the crystal in the required position and for micrometrical adjustments, the circle is provided with a tangent screw attached to the arm for the plate-holder. Crystal table and plate-holder as a whole can be turned about the same axis. A circle scale and nonius on the back of the spectrograph serve to give an approximate adjustment of the crystal to receive the X-ray pencil under the reflexion angle required. The plate-holder and slit stand are mounted on the same bed-plate, and a thick lead cover is laid over to prevent blackening through diffused rays. Calcite crystals alone have been used with this instrument. The measurement of the reflexion angle is carried out as follows. A fine slit (with gold edges) is adjusted, so that the normal from the rotating axis to the photographic plate passes through it. The crystal is placed on the table with its reflecting plane in the rotation axis. The crystal is then turned so that the normal slit-plate forms an angle with the crystal face approximately equal to the reflexion angle for the spectral line sought. This is done in two ways; in one case the plate-holder may be turned to the right side in order that the incoming pencil shall be reflected; in the other case a turning of the plate-holder to the left is necessary. This spectrograph is suitable for wave-lengths 0·5 Å.U. to 2·0 Å.U. The instrument has been tested on measurements of Cu$K\alpha_1$. In a previous paper, using the vacuum spectrograph, the value $\lambda=1537{\cdot}36XU$ was obtained; with the present instrument the value $\lambda=1537{\cdot}44XU$ is found; the difference 0·005% is attributed to a lack of information of the temperature-coefficient of the lattice constant of calcite. J. F. S.

The Radioactivity of the Water from the Principal Spring at Bagnoles-de-l'Orne and its Variations. P. Loisel (*Compt. rend.*, 1919, **169**, 791—792).—The water of Bagnoles contains from 22×10^{-12} to 109×10^{-12} grams of dissolved radium per litre, the mean value being 68×10^{-12} grams per litre. The amount of radium emanation in solution varies from 0·0002—0·0015 microcurie per litre. W. G

Application of the Thermionic Amplifier to Conductivity Measurements. R. E. Hall and L. H. Adams (*J. Amer. Chem. Soc.*, 1919, **41**, 1515—1525).—The use of an amplifier in conjunction with the telephone in the measurement of the resistance of solutions makes the determination of the point of balance on the bridge much simpler. Any ordinary telephone becomes a much more sensitive instrument with an amplifier than the best telephone without it. When a sensitive telephone is used, the current through the bridge may be reduced to a tenth of the value necessary without the amplifier, and the instrument will still have several times the sensitiveness it has without the amplifier. An electron tube may be used as a source of alternating current for conductivity measurements. Its advantages are its cheapness and the wide range of frequencies which may be obtained with it. A first harmonic is present in the current, which is noticeable at low frequencies, but which is not troublesome at a frequency of 1000 cycles or more. If, for any reason, it should be desired to use frequencies in conductivity measurements beyond the limit of the human ear, a telephone could still be employed to indicate the bridge balance by the use of the autodyne method. J. F. S.

Preparation of Conductivity Water. C. B. Clevenger (*J. Ind. Eng. Chem.*, 1919, **11**, 964—966).—The apparatus described is a modification of the Bourdillon still (T., 1913, **103**, 791); the steam, obtained from water containing phosphoric acid or potassium hydrogen sulphate, is led through a coil and trap, and then enters a vertical tin tube about 6 feet long, the inlet for the steam being at about the middle of the vertical tube. The latter is fitted with condensing jackets, one at the top and the other near the lower end, which is bent into the form of a trap and enters the containing vessel for the conductivity water. A current of pure air is admitted to the vertical tube through a side-tube just below the lower condensing jacket; this current of air ascends the vertical tube, mixes with the steam, and carries off any remaining impurities through the upper end of the tube. The various parts of the apparatus are made of tin-coated metal, and the upper end of the vertical tube is connected with absorption vessels for preventing the entrance of ammonia, etc. [See, further, *J. Soc. Chem. Ind.*, 1919, 928A.] W. P. S.

Behaviour of Electrolytic Ions in Solid Substances. Conductivity of Permutite Mixtures. A. Günther-Schulze (*Zeitsch. Elektrochem.*, 1919, **25**, 330—333).—The specific resistance and temperature-coefficient of twenty-one pure permutites have been determined by the method previously described (A., 1915, ii, 149). It is shown that in their preparation, in addition to an interchange of base, some permutites adsorb considerable amounts of salts. The specific conductivity of potassium–silver permutite and sodium–silver permutite of a series of compositions has been measured, and it is shown that in the former case the conductivity can be calculated according to the simple mixture

rule, whilst in the latter case this is only approximately true. On the assumption that the law of reciprocal influence of two salts with a common ion on the degree of ionisation holds, it follows that sodium, potassium, and silver permutite are dissociated to approximately the same extent. J. F. S.

Is the Electrical Conductivity of the Elements Conditioned by the Presence of Isotopes? F. H. Loring (*Chem. News*, 1919, **119**, 199—200. Compare this vol., ii, 384).—A theoretical paper in which various points dealt with in the previous paper (*loc. cit.*) are discussed in the light of the publications of other investigators. J. F. S.

Anodic Polarisation. II. A. Smits (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1349—1351).—An explanation of the phenomenon previously described (*ibid.*, 1918, **20**, 1121) is given. Iron can only exist in a state of internal equilibrium in a solution which contains no ferric ions. The presence of ferric ions disturbs the equilibrium, the more the greater the concentration of the ferric ions. The potential of iron is therefore less negative in a solution that contains ferric ions than in one which is free from ferric ions. In the solution with which the stated phenomenon was obtained, the iron consequently did not present the potential of internal equilibrium, but a less negative potential. In such a liquid, iron, when brought into solution, will change the concentration of the electrolyte in the neighbourhood of the electrode. The iron goes into solution exclusively as ferrous ion. During this anodic solution, the internal equilibrium is disturbed, as is indicated by the less negative potential, and, at the same time, the metal is surrounded by a liquid layer poorer in ferric iron than the rest of the solution. After the current has been broken, the iron approaches internal equilibrium with great rapidity, and on account of the decrease in ferric-ion concentration in its immediate neighbourhood, will exhibit a more negative potential than before polarisation. This state can, however, only persist for a short period, since the ferric ions diffuse from the outside into the boundary layer, and so the potential becomes less negative, and eventually reaches its initial value. J. F. S.

Electrical Characteristics of Pigment Colloids. Rudolf Keller (*Kolloid Zeitsch.*, 1919, **25**, 60—62).—In works of reference on colloids, among others in that of Zsigmondy, it is stated that basic colour substances in colloidal solution travel towards the cathode, acid substances towards the anode, under the influence of an electric current. The author finds that this is not a general rule, for alkaline solutions of methylene-blue and acid magenta travel to the anode and acid solutions of the same substances travel to the cathode. The reason for this behaviour is probably that in the first place pigment colloids, which have neither strong acidic nor strong basic characteristics, obtain their electric charges, according to Cohen's rule, by virtue of the ratio of the dielectric

constant compared with that of water, and in the second place from the electric charges of the dispersion medium. J. F. S.

Table of P_H·,H· and OH′ Values corresponding with Electromotive Forces determined in Hydrogen Electrode Measurements, with a Bibliography. Carl L. A. Schmidt and D. R. Hoagland (*Univ. California Pub. Physiol.*, 1919, **2**, 23—69).—The table includes values of P_H from 0·034 to 14·032. The bibliography of 467 titles covers the entire field of hydrogen-ion concentration up to 1919. The methods for the determination of hydrogen-ion concentration are reviewed.

Chemical Abstracts.

Discharge Electrolysis. Electrical Colloid Syntheses. V. Kohlschütter (*Zeitsch. Elektrochem.*, 1919, **25**, 309—323).—An electrical method for preparing colloidal metals is described which consists in electrolysing water with either direct or alternating current combined with a condenser circuit. The author terms the process "discharge electrolysis." Experiments are described in which colloidal copper is produced by the electrolysis of ordinary distilled water by means of direct current (96 volts) or alternating current (125/8000 volts), using two copper electrodes close together with a condenser in a parallel circuit. It is shown that when a discharge of at least 100 volts passes between two copper electrodes in distilled water, the cathode is disintegrated into fairly large particles, but if an oscillating parallel circuit is combined with the main circuit, the disintegration passes over, more or less completely, according to conditions, to the anode, and colloidal copper oxide is produced. Experiments with direct current show that an increasing capacity in the secondary circuit and a decreasing resistance in the main circuit increase the amount of disintegration, but, at the same time, the characteristic action of the oscillating circuit becomes more and more predominating. The disintegrated metal and the colloidal oxide are easily separated. The nature of the colloidal oxide depends on which of the two circuits predominates in its formation. The smaller the current strength and the capacity, the smaller are the colloidal oxide particles. The effect is produced because the electrolytic current covers the anode with a disperse oxide layer, and this is disintegrated by the spark discharge. When alternating current is used, the process is helped by a depolarising action of the cathodic component. J. F. S.

Auto-complexes in Solutions of Cupric Chloride and Cupric Bromide. Stewart Byron Watkins and Henry George Denham (T., 1919, **115**, 1269—1279).

Magneto-chemistry of Chromous and Oxychromic Salts. B. Cabrera and S. Piña de Rubies (*Anal. Fis. Quim.*, 1919, **17**, 149—167).—An account of a series of measurements of the magnetic susceptibility of solutions of chromous salts. The apparatus and the method of Quincke were employed. For the chromous

ion in sulphate and chloride solutions, the integral number 24 was obtained for the number of magnetons. The oxychromic salts of the formulæ $Cr_2O(SO_4)_2$ and Cr_2OCl_4, each in the violet and the green modification, were also studied. Integral numbers of magnetons for these complex cations were not obtained.

W. S. M.

Maximum Temperature [Limit]. Walther Jankowsky (*Zeitsch. Elektrochem.*, 1919, **25**, 325—328).—A theoretical paper in which, from a consideration of heat of reaction at medium temperatures, it is shown that this quantity is developed for the most part by a conversion of potential energy into heat. From this deduction, it follows that not only must an absolute zero of temperature exist, but that there must also be an absolute upper limit (maximum temperature). The absolute zero is defined as that temperature at which the energy content of a substance consists entirely of potential energy and at which a conversion of potential energy into heat is impossible. The maximum temperature is defined as that temperature at which the energy content consists entirely of heat and at which the conversion of heat into potential energy is impossible. All heat changes, inclusive of chemical reactions, must occur between these two temperature limits. In the neighbourhood of both points, the thermal properties of all substances approach the zero value. Both temperature limits are only reached asymptotically. J. F. S.

Investigation of Mewes' Law of the Relation between the Volume of a Gas and the Temperature. Rudolf Mewes and Ludwig Neumann (*Zeitsch. Sauerstoff. Stickstoff. Ind.*, 1919, **11**, 13—15; from *Chem. Zentr.*, 1919, iii, 149).—Some years ago, one of the authors proposed to replace Gay-Lussac's formula, $v_t = v_0(1+\alpha t)$, by the expression $v_t - x = (v_0 - x)(1+\alpha)^t$, or, approximately,

$$v_t = v_0(1+\alpha)^t,$$

where $\log(1+\alpha) = 0{\cdot}00111$. At temperatures above 0°, and within not too narrow limits, the results agree closely with those of Gay-Lussac's formula, but the discrepancies increase with decreasing temperature; at −182°, for example, the ratio of the density to that at 0° is about 3 according to Gay-Lussac and about 2 according to Mewes. Investigations by others have tended to confirm the older formula; the authors have therefore re-examined the behaviour of air, nitrogen, oxygen, and hydrogen with diminishing temperature, and have been led to the conclusion that sources of error are to be found in the previous arrangements of all investigators, including their own. To eliminate such sources (partial liquefaction and surface condensation of the difficultly liquefiable gases), the ratio of the liquid portion to the total amount must be ascertained, which could be accomplished mathematically. It is found, however, that they do not give a satisfactory explanation of the divergencies between the experimental and calculated results; particularly in the case of hydrogen, they

can only exercise a slight influence on the value of the specific heat. H. W.

The Specific Heat of Air at Ordinary and Low Temperatures. KARL SCHEEL and WILHELM HEUSE (*Zeitsch. Sauerstoff Stickstoff. Ind.*, 1919, **11**, 26—29; from *Chem. Zentr.*, 1919, iii, 148—149).—The previous determinations of the specific heat of air at low temperatures are confined to −77°, −102°, and −170°, and lead to the conclusion that the specific heat at atmospheric pressure is independent of the temperature. The authors' experiments have been performed with a specially constructed calorimeter, in which the loss of heat is reduced to very small dimensions. The apparatus and mode of experiment are fully described in the original. The authors find that the specific heat of air increases with decreasing temperature, and is approximately 5% greater at −183° than at the ordinary temperature. H. W.

Variation of the Specific Heat during Melting and the Heat of Fusion of some Metals. ITIRÔ IITAKA (*Sci. Rep. Tôhoku Imp. Univ.*, 1919, **8**, 99—114).—The specific heats of the elements bismuth, lead, tin, zinc, sulphur, and sodium have been determined at several temperatures, both above and below the melting points. It is shown that the specific heat undergoes a discontinuous change during melting, which is generally positive, but in some cases the change is negative. The following values have been obtained: bismuth, c_s 0·0338, c_l 0·0356, Mc_s 7·02, Mc_l 7·40; lead, c_s 0·0358, c_l 0·0340, Mc_s 7·43, Mc_l 7·04; tin, c_s 0·0662, c_l 0·0615, Mc_s 7·88, Mc_l 7·31; zinc, c_s 0·110, c_l 0·121, Mc_s 7·20, Mc_l 7·91; sulphur, c_s 0·200, c_l 0·199, Mc_s 6·41, Mc_l 6·39; sodium, c_s 0·330, c_l 0·347, Mc_s 7·59, Mc_l 7·98. The specific heat of the solid at the melting point is designated by c_s, that of the liquid at the same temperature by c_l, and the atomic heats by Mc_s and Mc_l respectively. The atomic heat is almost constant and independent of temperature for the liquid elements. The atomic heat at constant volume has been calculated for the temperatures 0°, 100°, 200°, 300°, and the melting point. The values at the melting point are: bismuth 6·90, lead 6·58, mercury 5·90, tin 7·40, and zinc 6·22. The latent heat of fusion has also been calculated from the experimental results, and the following values obtained: bismuth 12·24, lead 5·53, tin 13·38, zinc 23·1, sulphur 13·2, and sodium 26·0. J. F. S.

Calculation of the Latent Heat of Vaporisation from Critical Data. W. HERZ (*Zeitsch. Elektrochem.*, 1919, **25**, 323—324).—By means of the equations $L = p_k . T_s/T_k . d_k$ and $L = 2/3 . p_k/d_k$, the author shows that the latent heat of vaporisation of non-associated liquids may be calculated. The symbols have the following significance: L is the latent heat of vaporisation, T_s is the boiling point in degrees absolute, T_k and p_k the critical temperature and critical pressure respectively, and d_k is the critical density. The calculations have been made for twenty-

two organic liquids and three inorganic liquids, and it is shown that there is a moderate agreement between the calculated and experimental results. In the case of water and methyl alcohol, which are associated, there is a wide divergence between the calculated and experimental values, but in that of acetic acid, which is also associated, the two agree to within 10%. J. F. S.

A Vapour Pressure Equation. George W. Todd and S. P. Owen (*Phil. Mag.*, 1919, [vi], **38**, 655—660).—A mathematical paper in which the equilibrium of a vapour in contact with its liquid is considered on the assumptions that all vapour molecules striking the liquid surface penetrate it, and only those liquid molecules which have a velocity greater than a definite critical value, whatever their angles of impact with the surface, penetrate it and leave the liquid. Vapour-pressure equations $p=A\rho e^{-B/\theta}(1+B/\theta)$ and $p=A'e^{-B/\theta}(1+B/\theta)$ are deduced, in which p is the vapour pressure and ρ the density at a temperature θ, B is the collision frequency of a molecule of velocity c. The former equation is useful where the density values are known up to the critical temperature, and the latter for those cases where the density is only known over moderate ranges of temperature. The equations are tested in the case of water, mercury, benzene, bromine, and ethyl ether, where a fairly good agreement with experiment is found. The average kinetic energy of a molecule at the critical temperature (θ_c) is given by the expression $\frac{1}{2}mc_1^2=\theta_c/273(5{\cdot}5\times10^{-14})$ erg. A table of values of $\log A'$ and B obtained from vapour-pressure measurements is given for thirteen liquids, and it is shown that the value of B obtained from the critical temperature is one-third to one-fourth of the value obtained from the equation.

J. F. S.

Simple Method of Determining the Velocity of Sound in Gases and Vapours and the Density of Gases. P. Bräuer (*Zeitsch. physikal. Chem. Unterr.*, 1919, **32**, 1—6; from *Chem. Zentr.*, 1919, iii, 114—115).—The experiment is performed in thin-walled tubes, 2—3 cm. in diameter and at most 60 cm. long, which are filled with the gas or vapour. The note emitted when the tube is struck is matched by that of a monochord string, and the experiment is repeated with the tube full of air. The frequencies of the notes are inversely proportional to the lengths of the strings. The velocity of sound and the density of the gas are readily calculated. The procedure is as accurate as that proposed by Victor Meyer, and can be more rapidly carried out. H. W.

Absolute Determination of the Coefficients of Viscosity of Hydrogen, Nitrogen, and Oxygen. Kia-Lok Yen (*Phil. Mag.*, 1919, [vi], **38**, 582—596).—The absolute viscosities of hydrogen, nitrogen, and oxygen have been determined at 23·00° and 760 mm. pressure by Millikan's constant deflexion apparatus, previously described (Gilchrist, *Phys. Rev.*, 1913, **1**, 124; Harrington, *ibid.*, 1916, **8**, 738). The results obtained are: hydrogen, $\eta\times10^7=$

882·16 (20 expts.); oxygen, $\eta \times 10^7 = 2042{\cdot}35$ (20 expts.); and nitrogen, $\eta \times 10^7 = 1764{\cdot}80$ (21 expts.). An accuracy of 0·15% is claimed for the results. J. F. S.

Adsorption of Gases at Low and Moderate Concentrations. I. Deduction of the Theoretical Adsorption Isostere and Isotherm. II. Experimental Verification of the Form of the Theoretical Isosteres and Isotherms. A. M. Williams (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 287—297).—The theoretical form of the adsorption isostere is deduced and found to be $\log \alpha/c = B + A/T$, where A and B are functions of α alone. The theoretical form of the adsorption isotherm is found to be $\log \alpha/c = A_0 - A_1\alpha$, where A_0 and A_1 are functions of the temperature only. These equations are tested by means of the data of various observers on the gases, argon, methane, carbon dioxide, ammonia, nitrogen, and carbon monoxide. A satisfactory agreement is found in the case of the former equation for gases above or near the critical temperature. In the latter case satisfactory agreement is found up to moderate adsorptions of gases above their critical temperature. J. F. S.

Adsorption of Gases at Low and Moderate Concentrations. III. Experimental Verification of the Constants in the Theoretical Adsorption Isostere. A. M. Williams (*Proc. Roy. Soc.*, 1919, [*A*], **96**, 298—311. Compare preceding abstract).—The constants of the equation for the theoretical adsorption isostere are deduced from the observations of many observers for the gases argon, ethylene, carbon dioxide, methane, carbon monoxide, and nitrogen. The form of theoretical adsorption isostere has been determined at zero concentration for the above-named gases above the critical point. The relationship among the constants is in good agreement with the theory based on the existence of a thin surface layer. The range of molecular attraction is determined and found to vary from 3·2 to $4{\cdot}1 \times 10^{-8}$ cm. J. F. S.

Theory of Adsorption of Electrolytes. The Adsorption of Organic Dyes. Leonor Michaelis and Peter Rona (*Biochem. Zeitsch.*, 1919, **97**, 57—84).—The salts of basic and acid dyes have been employed in the study of adsorption by various substances. In the case of charcoal the cations and anions are adsorbed in equivalent proportions. Slight deviations from this principle can be explained by the impurity of the charcoal. When insoluble salts are used as adsorbents there is an exchange of anions or cations between the adsorbents and the substance adsorbed. Insoluble acid or basic oxides have shown no perceptible adsorbing capacity. In no case was a "hydrolytic" adsorption of the salts observed, that is, where the salts were split into acid and base, and the adsorption of one ion only took place. The nature of the adsorption capacity of carbon is discussed. S. S. Z.

Adsorption of H- and OH-Ions and the Ions of the Heavy Metals by Charcoal. Peter Rona and Leonor Michaelis (*Biochem. Zeitsch.*, 1919, **97**, 85—97).—The H- and OH-ions are

adsorbed by charcoal to the same extent. The amount of mercuric chloride adsorbed by charcoal may, in the presence of chlorides, be diminished by as much as 60%. S. S. Z.

Electrification of Water and Osmotic Pressure. Jacques Loeb (*J. Gen. Physiol.*, 1919, **2**, 87—106).—It is shown for the amphoteric electrolytes, aluminium hydroxide, and gelatin, that in the presence of an acid salt water diffuses through a collodion membrane into a solution of these substances as if its particles were negatively charged, whilst water diffuses into solutions of these electrolytes, when they exist as salts of univalent or bivalent metals, as if the particles of water were positively charged. The turning point for the sign of the electrification of water seems to be near or to coincide with the isoelectric point of these two ampholytes, which is about $2 \times 10^{-5} N$ for gelatin and $10^{-7} N$ for aluminium hydroxide.

Apparently positively charged water diffuses with less rapidity through a collodion membrane into a solution of calcium or barium gelatinate than into a solution of lithium, potassium, sodium, or ammonium gelatinate of the same concentration of gelatin and hydrogen ions, and negatively charged water diffuses with less rapidity through a collodion membrane into a solution of gelatin sulphate than into a solution of gelatin chloride or nitrate of the same concentration of gelatin and hydrogen ions.

If osmotic pressure is defined as the additional pressure on the solution required to cause as many molecules of water to diffuse from solution to the pure water as diffuse simultaneously in the opposite direction through the membrane, it follows that the osmotic pressure cannot depend only on the concentration of the solute, but must also depend on the electrostatic effects of the ions present, and that the influence of the ions on the osmotic pressure must be the same as that on the initial velocity of diffusion. This assumption was tested in experiments with gelatin salts, for which a collodion membrane is strictly semipermeable, and the tests confirmed the expectation. J. C. D.

Hydrogen and Hydroxyl Ion Equilibria in Solutions. II. W. Löffler and K. Spiro (*Helv. Chim. Acta*, 1919, **2**, 533—550. Compare Asher and Spiro, *Ergb. Physiol.*, 1909, **8**, 254).—From experiments, carried out by the indicator method, on the changes in the hydroxyl and hydrogen-ion concentration in solutions of glycine brought about by neutral substances of physiological importance, such as glycerol, dextrose, and ethylene glycol, it is shown that these substances are capable of forming complex salts. This is seen particularly in the case of glycine. Such solutions, which are non-sensitive to a change in their alkalinity, change their concentration of hydrogen and hydroxyl ions by shaking with animal charcoal in the sense that they approach neutrality. The adsorption by charcoal is to be regarded as a process of solution, and it is shown that a different decomposition of acid salts in aqueous solution is brought about by shaking with animal charcoal. J. F. S.

[Behaviour of Non-aqueous Solutions of Salts.] R. BEUTNER (*Zeitsch. Elektrochem.*, 1919, **25**, 328—329, 329—330. A. THIEL, *ibid.*, 329).—Polemical. Beutner answers Thiel's criticism (this vol., ii, 388) of his paper (this vol., ii, 263). In a second paper Thiel further criticises Beutner's conclusions, and in a third paper Beutner gives a final reply to Thiel. J. F. S.

Crystallisation Phenomena in Formaldehyde-Gelatin Jellies. W. MOELLER (*Kolloid. Zeitsch.*, 1919, **25**, 67—74).—The crystallisation of formaldehyde gelatin jellies has been experimentally studied. It is shown that the crystallisation phenomena (formation of sphäro-crystals) are to be attributed to the orienting influence of the formaldehyde condensation and polymerisation products on the α-gelatin micellæ. In the observed spherical crystal formation the individual micellæ are arranged radially in the form of concentric spherical sheaths, and behave optically as a crystalline drop. The numerous forms which differ from the above are attributed to a deformation brought about by the tensions set up while the jelly is drying, whereby the arrangement of the micellæ approaches more and more to a fibrous structure. Sphäro-crystals produced by varying the experimental conditions often exhibit this fibrous structure. J. F. S.

Coagulation. I. The Velocity of Gelation and Hydrolysis of Gelatin Sol. RINNOSUKE SHŌJI (*Biochem. J.*, 1919, **13**, 227—238).—The equation $\eta-\eta_i=\mu t/1+(\mu/\lambda)t$ is given, which represents the change in viscosity of gelatin sol with respect to time in the early stages of gelation, and the bearing of this equation on the nature of gelation is discussed at some length.

Another equation, $2k\tau=1/(\eta_i-\eta_{i\infty})^2-1/(\eta_{i0}-\eta_{i\infty})^2$, is given which represents the change in viscosity of gelatin sol with respect to time in the course of its hydrolysis caused by heating. J. C. D.

Coagulation Process [of Colloids]. H. R. KRUYT and JAC. VAN DER SPEK (*Kolloid Zeitsch.*, 1919, **25**, 1—20).—The coagulation of arsenic sulphide and ferric hydroxide sols has been investigated. It is shown that the relationship between coagulation value and the colloidal concentration for arsenic sulphide sols varies as follows: the coagulation value for a univalent precipitating ion increases with increasing dilution, for a tervalent ion it decreases, and for a bivalent ion there is a slight decrease. The reduction of the degree of dispersion by boiling or by a change in the original concentration leads to an augmentation of the coagulation value for potassium and barium ions, but to a reduction for aluminium ions. These phenomena may be explained by the hypothesis that the colloidal particles may combine as they approach one another through their Brownian movements. The reduction of the total surface conditions a reduction of the quantity of electrolyte necessary to reach a definite adsorbed quantity. Dilution and a reduction in the dispersity cause a separation of the particles and

reduce the chances of their collision, and under these conditions a smaller charge is necessary for their coagulation. Similar experiments were made with ferric hydroxide sol, but here both sodium hydroxide and disodium phosphate behave irregularly. J. F. S.

Colloidal Processes in the Setting of Plaster. Structure of Plaster of Paris. I. Traube (*Kolloid. Zeitsch.*, 1919, **25**, 62—66).—The velocity of the setting of the hemihydrate of calcium sulphate has been investigated, and the influence of the addition of salts, acids, bases, and neutral substances to the soft plaster on the rate of setting has been observed. Ten grams of calcium sulphate were rapidly mixed with stated quantities of water or solutions of other substances, the mixture poured on to a glass plate, and the time noted when it had completely set. With 4 c.c. of 0·5*N*-potassium chloride, setting occurred almost instantaneously, with 5 c.c. in 2·5 minutes, with 7 c.c. in 4 minutes, with 15 c.c. the mixture had not set in 40 minutes. Using 7 c.c. of saturated potassium chloride solution, setting occurred in 12 minutes; 7 c.c. of *N*/2-solution required 4·5 minutes, 7 c.c. of 0·25*N* required 5·5 minutes, and 7 c.c. of *N*/16 19 minutes. There is, therefore, a maximum setting velocity for medium concentrations. In experiments with other salts, it is shown that the influence of the anion is very small, but that of the cation is all-important. The order in which the cations influence the setting is the reverse of the order in which they precipitate colloids from solutions; thus the univalent cations accelerate the setting most. From these experiments, it is concluded that the combination of the hemihydrate of calcium sulphate with water is brought about in the first place by gel formation. A similar series of experiments was made with 7 c.c. of various acids in *N*/2-concentration. The order of setting from the most rapid is hydrochloric acid, oxalic acid>sulphuric acid>trichloroacetic acid > tartaric acid > boric acid > phosphoric acid > dichloroacetic acid>chloroacetic acid>acetic acid>propionic acid >citric acid. The addition of 7 c.c. of *N*/2-potassium hydroxide effected setting in about the same time as hydrochloric acid. Non-conductors, such as chloral hydrate, amyl alcohol, propionitrile, mannitol, paracetaldehyde, methyl alcohol, and methyl ethyl ketone had no influence on the rate of setting. Gelatin and gums retarded the rate of setting. By allowing ferric chloride to diffuse through the set plaster towards potassium ferrocyanide which is diffusing in the opposite direction, structures of the same nature as the protoplasm structure are obtained. Agate structures and others of both geological and physiological interest have also been obtained. The author's experiments confirm in every detail the views on the nature of the setting of cements put forward by Cavazzi (A., 1913, ii, 136). J. F. S.

Molecular Mechanism of Colloidal Behaviour. II. The Swelling of Fibrin in Alkalis. Richard C. Tolman and Russel S. Bracewell (*J. Amer. Chem. Soc.*, 1919, **41**, 1503—1510. Compare Tolman and Stearn, this vol., ii, 101).—The swelling of

fibrin in solutions of sodium hydroxide, potassium hydroxide, and ammonia of various concentrations, and also of similar solutions containing potassium chloride, potassium sulphate, and sucrose has been investigated. It is shown that the swelling in solutions of sodium and potassium hydroxides reaches a maximum at very low concentrations—less than $N/20$; in the same way, the adsorption of alkali reaches a maximum at low concentrations, and a further increase in the concentration of the alkali brings about no change in the adsorption, but a reduction in the amount of swelling. In the case of ammonia solutions, it is shown that both the amount of swelling and the adsorption increase with increasing concentration up to $0{\cdot}8N$ without reaching a maximum. The addition of neutral salts reduces the swelling in the same way as increase in the concentration of the alkali itself after the maximum has been reached, and also increases the adsorption. Sucrose has no effect on the swelling of fibrin, but water is adsorbed from the solution by the fibrin. J. F. S.

Molecular Mechanism of Colloidal Behaviour. III. Chemical Nature of the Adsorption of Acids and Alkalis by the Protein Molecule. Russel S. Bracewell (*J. Amer. Chem. Soc.*, 1919, **41**, 1511—1515. Compare preceding abstract).—A theoretical paper in which it is shown that the acid-adsorbing power of proteins is mainly due to the free amino-groups present, that is, adsorption consists in the formation of weak compounds between the amino-group and the acid. Attempts to formulate a similar hypothesis for alkali adsorption were unsuccessful. J. F. S.

Colour of Colloids. VIII. Wilder D. Bancroft (*J. Physical Chem.*, 1919, **23**, 445—468. Compare this vol., ii, 324).—A continuation of the previously published discussion. In the present paper, absorption colours, colours of turbid media, prismatic dispersion colours, grating colours, and colours of thin films are discussed in their relationships with the colour of birds and butterflies. J. F. S.

Colloidal Electrolytes: Soap Solutions as a Type. James William McBain, (Miss) Mary Evelyn Laing, and Alan Francis Titley (T., 1919, **115**, 1279—1300).

The Degree of Hydration of the Particles which Form the Structural Basis of Soap Curd, Determined in Experiments on Sorption and Salting Out. James William McBain and (Miss) Millicent Taylor (T., 1919, **115**, 1300—1308).

Simultaneous or Successive Chemical Decompositions Provoked by Physical Agents. J. A. Muller (*Compt. rend.*, 1919, **169**, 793—794).—In simultaneous decompositions of the first order, the ratios of the two coefficients of decomposition, at the end of any given time, are equal to the ratios of the corre-

sponding velocity constants. The subject is discussed mathematically, and the equations given, together with the results of chemical analyses, provide a means of determining the nature and order of the changes produced in pyrogenic decompositions. W. G.

The Interaction of Chlorine and Hydrogen. The Influence of Mass. David Leonard Chapman and John Reginald Harvey Whiston (T., 1919, **115**, 1264—1269).

Comparison of the Temperatures of Explosion calculated from Specific Heats with the Temperatures of Explosion calculated from Explosive Pressures. Henri Muraour (*Compt. rend.*, 1919, **169**, 723—726).—As the result of experiments with mixtures of tolite and ammonium nitrate, it is shown that the explosion temperatures, as calculated from the specific heats of Mallard and Le Chatelier or of Sarrau, are markedly higher than the figures obtained by calculation from the manometric tables, except where the temperatures are above 3000°. The results obtained by either method in the region 1500—1700° are certainly below the actual temperatures. The results, as calculated from the manometric pressure in this region, are so low as to indicate either that the value of the pressure must be modified or that the law used for expressing the compressibility of gases at high temperatures and pressures is incorrect. Over the temperature range 1300—2700° the temperatures, calculated from Schreber's specific heats, are in accord with the temperatures calculated from the pressure tables of the French research laboratories. W. G.

Ignition of Gases by Hot Wires. W. M. Thornton (*Phil. Mag.*, 1919, [vi], **38**, 613—633).—The ignition of the gases hydrogen, methane, ethane, pentane, ethylene, carbon monoxide, coal gas, and vapours of methyl alcohol, ethyl alcohol, diethyl ether, and benzene in air by electrically heated wires of platinum, nickel, iron, tungsten, molybdenum, gold, and silver of various diameters and at various temperatures has been experimentally investigated. It is shown that ignition by hot wires occurs when the generation of heat per unit length has reached a certain definite value. At low temperatures, this is removed by convection, when a steady state is reached, and is almost independent of the diameter of the wire. Ignition is independent of gas pressure, of the heat of combustion of the mixture, of the proportion of gas present, and for any given metal, independent of the nature of the combustible molecule so far as it is affected by change of diameter, hydrogen and platinum being exceptions. That is, since previous heating of the gas does not affect ignition temperatures, it is, on the whole, independent of every external physical or chemical variable. The source of ignition must therefore be sought in some phenomenon depending strictly on the rate of generation of heat by the passage of the current, but occurring, if not within the surface layer of the metal itself, so near to it that the ordinary gas laws are not

operative. Oxygen is the only active component of all the mixtures, and it can be inferred that the mechanism of hot wire ignition is an attack on oxygen either within the wire or by positive ions of combustible gas just ejected from it, for the temperatures at which surface action begins are lower than those which start combination of gases separately heated to a point at which they explode on mixing. Electric and magnetic fields have no influence on surface combustion observable by the phenomena of ignition. Compared with spark ignition, hot wire ignition is singularly constant in type. J. F. S.

The Determination of Ignition-temperatures by the Soap-bubble Method. Albert Greville White and Tudor Williams Price (T., 1919, **115**, 1248—1264).

Indirect Analysis of Gas Hydrates by a Thermodynamic Method and its Application to the Hydrate of Hydrogen Sulphide. I. and II. F. E. C. Scheffer and G. Meyer (*Proc. K. Akad. Wetensch. Amsterdam*, 1919, **21**, 1204—1212, 1338—1348). —In earlier papers (Scheffer, A., 1911, ii, 264, 870) it is shown that in solutions of hydrogen sulphide a four-phase equilibrium exists between a hydrate, two liquid phases (water and hydrogen sulphide), and gas. The analysis of the hydrate leads to a water content between 5·1 and 5·4 molecules per molecule of hydrogen sulphide. It is likely that the accepted value $5H_2O$ is not correct, and, with the object of determining the true composition, the authors have developed, on thermodynamical considerations, a method of indirectly ascertaining the composition of such hydrates. The method is briefly as follows. A binary system is taken of which one component, A, is gaseous over a definite temperature range, and the second, B, is near its melting point, and is not markedly volatile. On increase of pressure, a solid compound can form from the gas A and the solid B. In the melted component B, the gas is soluble neither as such nor as compound. In the equilibria set up, the component A appears as a gas (G) and bound in the compound S; the component B occurs free as solid, S_B, and liquid, L, and bound in the compound S. The three-phase lines S_BLG and SS_BL coincide with the melting-point line of B. The transformation is indicated by the change $S_B \rightleftarrows L$ on both three-phase lines, and is the same as on the melting-point line of pure B. The triple point of B lies near the T axis; the sublimation and boiling-point line of B practically coincides with the I axis. If the compound is indicated by AB_n, the transformations on the two other three-phase lines are indicated by $AB_n \rightleftarrows A+nB-E_1$ (on SS_BG) and $AB_n \rightleftarrows A+nB-E_2$ (on SLG). The difference of the two energies E_1 and E_2 is equal to the heat of fusion of n molecules of B. $E_2-E_1=nQ$ when the heat of fusion of B is Q per molecule. Making use of the Clapeyron equation, the value of E_2-E_1 can be determined if the three-phase lines $SS\,G$ and SLG are known. This method is applied to the system hydrogen sulphide–water, and the lines SS_BG and SLG are experimentally determined, and from

the data thus obtained the value of n is found to be 6. Hence the crystalline hydrate of hydrogen sulphide is $H_2S,6H_2O$.

J. F. S.

Theory of the Velocity of Reaction in Gases. Karl F. Herzfeld (*Ann. Physik*, 1919, [iv], **59**, 635—667; *Zeitsch. Elektrochem.*, 1919, **25**, 301—304).—A theoretical paper in which the velocity of reactions of the first and second order is discussed mathematically. In an historical introduction, the work of Trautz (A., 1909, ii, 557, 651), among others, is discussed. It is shown that, in developing a systematic conception of gas reactions, the introduction of a retardation is helpful. That is, a condition based on the consideration of whether an atom can react directly or whether it must first break away from an existing combination before reaction is possible. In exothermic reactions with one or no retardation, every collision of the molecules is operative, independently of the temperature, whilst with two retardations only a small fraction of the collisions is operative, and these are dependent on the temperature. In the case of endothermic reactions, only one example of a retardation is known, namely, the formation of hydrogen bromide; here it is shown that, for a collision to be operative, the kinetic energy, which depends on the opposing velocities of the colliding particles, must be greater than the heat of the reaction. The influence of the internal energy makes itself obvious, inasmuch as only a definite proportion of the reacting substances can be converted into the products of the reaction. Therefore in exothermic reactions the number of operative collisions is to be multiplied by a factor which depends on the internal specific heat. The reaction formulæ deduced are applied to the work of Bodenstein (A., 1899, ii, 637) and Lind (A., 1907, ii, 76) on the formation of hydrogen bromide, and very good agreement is shown to exist.

J. F. S.

The Velocities of Combination of Sodium Derivatives of Phenols with Olefine Oxides. II. David Runciman Boyd and (Miss) Doris Feltham Thomas (T., 1919, **115**, 1239—1243).

The Rate of Hydrolysis of Methyl Acetate by Hydrochloric Acid in Water-Acetone Mixtures. George Joseph Burrows (T., 1919, **115**, 1230—1239).

Kinetics of Reactions with Substituted Malonic Acids. A. L. Bernoulli and W. Wege (*Helv. Chim. Acta*, 1919, **2**, 511—532).—The kinetics of the scission of carbon dioxide by heat from malonic acid or methyl-, ethyl-, allyl-, benzyl-, phenyl-, diallyl-, dimethyl-, methylethyl-, diethyl- and dipropyl-malonic acids have been studied at 100°. The formation of acetic acid from an aqueous solution of malonic acid, over the temperature range 75—110°, is a strictly unimolecular reaction. By means of graphic extrapolation, it is shown that the lower limit of measurable change

lies at 66°. With the single exception of dipropylmalonic acid, in which case the value of k is not satisfactory, it is shown that all the substituted malonic acids are decomposed at 100° in aqueous solution, according to a unimolecular equation. Substituents, in the malonic acids, with either one or more double bonds, increase the velocity of decomposition, whilst substituents without double bonds reduce the rate of decomposition. The accelerating action of the double bond increases with the number and also with the nearness to the methylene group of the malonic acid; thus, the phenyl group accelerates the velocity more than the benzyl group. The entrance of a second substituent, similar or dissimilar, strongly decreases the rate of decomposition; thus, diallylmalonic acid decomposes with about half the velocity of allylmalonic acid. A parallelism is shown between the thermal stability of these substances (measured by the heat of formation) and the kinetic stability (measured by the reciprocal of the reaction velocity).

J. F. S.

The Rhythmic Evolution of Carbon Monoxide and the Constant of Accumulation. Tokiharu Okaya (*Proc. Phys. Math. Soc. Japan*, 1919, [3], **1**, 43—51).—The author has previously suggested that in the case of the rhythmic precipitation of silver chromate in gelatin, there must exist certain relations between the concentrations of the reacting ions to determine the physical state at the moment of precipitation, and concluded that to precipitate silver chromate it is only necessary that the amount of "accumulation product" of the ions should attain a definite value, H^1, which is constant throughout. In the present paper, the phenomenon of the rhythmic evolution of carbon monoxide produced by the dehydration of formic acid by sulphuric acid is satisfactorily explained by the notion of the "accumulation product." It is also shown that the reaction is one of the first order. The author points out that the existence of the quanta in natural phenomena is not limited to energy only. The present case and Liesegang's phenomena are but examples of such types of natural phenomena.

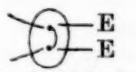
Chemical Abstracts.

Size and Shape of the Electron. Arthur H. Compton (*Physical Rev.*, 1919, **14**, 20—40).—Assuming as proved that the amount of radiation of short wave-length scattered by various elements is proportional to the atomic number of the element, and accepting Thomson's assumption that the electron is a point charge, the scattered energy should be as great as that calculated from the Thomson equation. Actually, it is considerably less, sometimes as low as one quarter of the theoretical value. Unless a pulsation theory for these rays is abandoned, the discrepancy can only be explained on the assumption that the electron is comparable in magnitude with the wave-length of the shortest rays, or 2×10^{-10} cm. Three types of electrons are suggested, and the scattering is calculated for each type. All three satisfactorily fulfil the requirements. Type I, rigid spherical shell; type II,

flexible spherical shell; type III, flexible spherical ring. On still another count, a point charge electron is inadequate to account for the fact that emergent scattered radiation is more intense than incident radiation. It is necessary to assume an independent rotational activity of the electron, which type III above seems best suited to admit. CHEMICAL ABSTRACTS.

Valency Centres. O. HINSBERG (*J. pr. Chem.*, 1919, [ii], **99**, 232—238).—An extension of ideas previously advanced (A., 1916, i, 725; 1917, ii, 173, 461; 1918, ii, 106).—The theory deals with the elements of the first, second, fourth, sixth, and eighth groups of the periodic system, and it is assumed that one valency centre is present in the first four elements of each series and two valency centres in the four succeeding elements. The discontinuity of the physical properties of the elements in a series is conditioned by the occurrence of the second valency centre from the fifth group onwards, which causes a marked depression in melting and boiling points. In the formation of compounds with negative elements, the total valency of the elements of the fifth to seventh groups is utilised, whilst with positive elements or groups only the differential valency is used; the occurrence of elements of no valency appears to be merely an extension of the process of equalisation of the valencies of the two centres, the commencement of which is already apparent in the fifth to seventh groups. The ability to form ions, which is proper to many elements of the sixth and seventh groups, is probably due to the tendency of the atoms to form a particularly stable system by internal equalisation, in which four electrons are attached to each nucleus, or eight electrons are contained in a ring. The capability of forming onium compounds, as exhibited by nitrogen, sulphur, iodine, etc., depends on the presence of two valency centres, and therefore occurs solely in the right half of the periodic system. The equivalence of the sulphur atom to the –CH:CH– group in the formation of ring compounds (for example, thiophen and benzene) is explained by the formulæ:

CH:CH and



S (in thiophen)

in which the two hydrogen atoms of the group CH:CH are replaced in the sulphur atom by two valency electrons (E), which are not compensated within the atom.

A number of cases among sulphur compounds are known, in which the isomerism can only be explained with difficulty if the presence of a single valency centre in the sulphur atom is assumed; if, however, two valency centres are present, the difficulty is removed. Thus the isomeric β-naphthol sulphides, m. p.'s 216° and 152° respectively, can be formulated:

$OH\cdot C_{10}H_6—\cdot\ \cdot—C_{10}H_6\cdot OH$ and $OH\cdot C_{10}H_6—\overset{\cdot\cdot}{:}—C_{10}H_6\cdot OH$.

The molecular complexity of the metalloids can be explained by

assuming that the partial equalisation of the two valency systems which occurs within the atoms can also take place between different atoms. H. W.

Isomorphism, Isosterism, and Co-valence. Irving Langmuir (*J. Amer. Chem. Soc.*, 1919, **41**, 1543—1559).—The octet theory of valency indicates that if compounds having the same number of atoms have also the same total number of electrons, the electrons may arrange themselves in the same manner. In this case the compounds or groups of atoms are said to be isosteric. Such compounds should show remarkable similarity in their physical properties, that is, in those properties which do not involve a separation of the atoms in the molecule. Thus O^{--}, F^-, Ne, Na^+, and Mg^{++} are isosteric, as also are $N_2{\cdot}CO{\cdot}CN^-$ and CH_4 and NH_4^+. In cases where isosteric groups have the same electric charges the properties are directly comparable; thus, N_2 and CO, N_2O and CO_2, KN_3 and HCNO are nearly alike in all their physical properties. When the charges are dissimilar the similarity may manifest itself between properly chosen compounds, thus, KNO_3 and $CaCO_3$. The following cases of crystalline isomorphism are predicted by the octet theory and found to be in accordance with experimental observation: NaF and MgO, KN_3 and KNCO, KNO_3 and $SrCO_3$, $KClO_4$ and $SrSO_4$, $NaHSO_4$ and $CaHPO_4$, $MnSeO_4,2H_2O$ and $FeAsO_4,2H_2O$. Many other pairs are predicted, but have not yet been experimentally investigated. The theory of isosterism makes the deduction of certain relationships a very simple matter. Thus since argon is an isostere of the potassium ion, and methane is an isostere of the ammonium ion, it follows that the potassium and ammonium ions must have similar properties because argon and methane are nearly alike in physical properties. Similarly, the relationship between argon and nitrogen enables the tracing of an equally close relationship between cyanogen and chlorine ions. The experimental data prove that the crystalline form of substances depends on the structure as given by the octet theory, thus indicating that this theory gives a true picture of the constitutions of crystalline solids. The following conclusions are drawn: (1) the co-valency of sodium, potassium and chlorine (in chlorides) is zero. (2) The co-valency of the central atom is 4 in nitrates, carbonates, sulphates, perchlorates, phosphates, permanganates, chromates, selenates, and borofluorides. (3) Carbonates and sulphites are not isomorphous, the co-valency of the central atom being 4 and 3 respectively. (4) Nitrates and chlorates are not isomorphous, the co-valency of the chlorine being 3 in chlorates. J. F. S.

New Hypotheses as to Different States of Matter. N. T. Bacon (*J. Physical Chem.*, 1919, **23**, 469—477).—A theoretical paper in which it is shown that in the solid and liquid conditions matter is virtually incompressible, although under very high pressure, but constantly increasing in volume with increasing temperature, and for the liquid state with this condition continuing up to the critical point, except that near the critical point the apparent

compressibility of the liquid phase may be increased by solution of vapour molecules. The molecule, therefore, is constantly increasing the diameter of its sphere of influence as temperature increases up to the critical point. At this point the spheres of influence of the molecule of liquid and of vapour have the same size, since both forms of matter occupy the same space and have the same density. At the critical point the volatile form is at the dividing line between a saturated vapour and a true gas, and the vapour cannot act as a true gas because the spheres of influence of its molecules are in three dimensional contact, thus precluding translatory motion. Although the molecules in the liquid state continue to increase the dimensions of their spheres of influence with advancing temperature in spite of increasing pressure, nevertheless gaseous molecules can be materially compressed so as to occupy a smaller volume than at the critical point even at temperatures well above the critical temperature. Hence the spheres of influence of a true gas decrease with increasing temperature so as to allow a free path and thus cause them to follow Boyle's Law. The effect of the dissolved barium sulphate in a saturated aqueous solution is considered. Here a single molecule of barium sulphate (that is, one barium ion and one sulphate ion) so influences 10,000,000 water molecules that they are incapable of dissolving more barium sulphate, and imparts to the water a much higher conductivity; all this when the barium sulphate in solution can only come into contact with a small fraction of the water molecules. The author considers that the solution of barium sulphate up to its saturation point brings about a virtual expansion of the water molecules so as practically to fill up all the intermolecular spaces in the solvent and consequently leave no further room for additional barium sulphate. The conductivity of the barium sulphate solution he attributes to the barium sulphate breaking up into an enormous number of electrons, each having the characteristic periodicity of barium sulphate, and these so permeate the solvent that each molecule of this is in some way in contact, periodically at least, with such particles, so as to maintain an equilibrium relation. In the case of hydrolysis the complicated periodicity of the salt becomes too extended, so that part of the solute loses coherence and the fractions revert to their simpler, although related, periodicity, each in its own condition as if the other were not present. J F. S.

Automatic Mercury Pump, with Device for Collecting the Aspirated Gases. A. Beutell and P. Oberhoffer (*Chem. Zeit.*, 1919, **43**, 705—706).—In the mercury pump previously described (A., 1911, ii, 105) the authors have introduced a vessel at the base of the tubes for collecting the gases drawn off, which are then passed into a measuring burette and an Orsat gas-analysis apparatus. The speed of the pump has been increased by allowing the mercury to drop through two tubes, and the device for preventing fracture of the tubes by the falling mercury has been modified.

W. J. W.

Inorganic Chemistry.

Reaction between Hydrogen and Bromine. J. A. Christiansen (reprint from *D. K. Danske Videnskabernes Selskat. Math. fys. Medd.*, 1919, **1**, 14).—A theoretical paper in which it is shown from the experiments of Bodenstein and Lind (A., 1907, ii, 76) on the formation of hydrogen bromide that the reaction occurs as a result of the following changes: $Br + H_2 = HBr + H$ (primary reaction) and $H + Br_2 = HBr + Br$ or $H + HBr = H_2 + Br$, and consequently the dissociation of hydrogen bromide takes place with the reaction $Br + HBr = Br_2 + H$ as the primary change, and is followed by the same secondary reactions as above. It is also shown that the existing experimental data do not exclude the possibility of the formation and dissociation of hydrogen iodide according to the same scheme. The numerical results of Bodenstein and Lind have been used to calculate the critical energy of the process $Br + HBr = Br_2 + H$ and the value 43,700 cal. obtained. The results are generally considered, and it is concluded that in respect of the heat of dissociation of hydrogen, Langmuir's value, 84,000 cal. (A., 1915, ii, 249), is probably not irreconcilable with Bohr's theoretical value, 62,000 cal. (A., 1913, ii, 1045). A method of illustrating the above-mentioned reaction by means of models of atoms and molecules similar to those of Bohr is indicated. J. F. S.

Periodic Acid and Periodates. Arthur Rosenheim and Else Loewenthal (*Kolloid. Zeitsch.*, 1919, **25**, 53—60).—The periodates of sodium, lithium, ammonium, and guanidine have been investigated. The hydrogen-ion concentration of $N/20$-solutions of H_5IO_6, NaH_4IO_6, and $Na_2H_3IO_6$ was determined by Sörensen's indicator method with the object of finding the most suitable indicator for use in titrating periodic acid with sodium hydroxide. The hydrogen-ion concentrations found are respectively 6×10^{-3}, $4{\cdot}05 \times 10^{-7}$, and $6{\cdot}5 \times 10^{-10}$. It is shown that, using methyl-orange as indicator, periodic acid can be quantitatively converted by titration into NaH_4IO_6, and that using thymolphthalein as indicator it is converted into $Na_2H_3IO_6$. The solubility of $Na_2H_3IO_6$ is determined at various temperatures, and the following values in grams per 100 grams of solution obtained: 0°, 0·104; 25°, 0·157; 40°, 0·187; 100°, 0·434. Shaking with 10N-sodium hydroxide solution converted this salt into $Na_3H_2IO_6$. A number of experiments, designed to ascertain whether the sodium periodates adsorb sodium hydroxide, were carried out at 17° by shaking periodic acid with a concentrated solution of sodium hydroxide. The experiments show that neither of the sodium periodates mentioned exhibit any colloidal properties, and that these are the only sodium periodates capable of existence in aqueous solution. On the addition of 1 mol. of periodic acid to 2 mols. lithium hydroxide solution a white precipitate is formed which immediately dissolves; the solution, on warming, yields a

white precipitate consisting of microscopic spherules, which on analysis is shown to consist of $Li_3H_2IO_6$. The mother liquor on keeping deposits small, white, six-sided bipyramids of $Li_2H_3IO_6$. Attempts to prepare $LiIO_4$ and Li_5IO_6, compounds described by Rammelsberg, failed. The two lithium salts were examined as to the power of adsorption as in the case of the sodium salts, and it is shown that absorption compounds are formed up to the ratio $Li_2O/I_2O_7=5\cdot39$. The two ammonium periodates $(NH_4)_2H_3IO_6$ and NH_4IO_4 previously described by Rammelsberg (*Ann. Phys. Chem.*, 1868, **134**, 379) were obtained, and a further compound, $(NH_4)_3H_7(IO_6)_2,2\frac{1}{2}H_2O$, was also obtained. The last compound was prepared in rectangular crystals by shaking periodic acid with an excess of 25% ammonia at 140° for several hours. Two guanidine periodates, $(CN_3H_6)_3H_2IO_6$ and $(CN_3H_6)_2H_3IO_6$, were obtained by treating periodic acid with guanidine. Both substances are very sparingly soluble, white, crystalline compounds. The molecular conductivity, boiling point, and freezing point of a number of solutions of periodic acid have been determined. The conductivity determinations show that periodic acid is of medium strength, whilst the boiling-point determinations indicate that it dissociates into two ions, and the freezing-point determinations show that a 5% solution is much less dissociated, and that in a 12—20% solution polymeric periodic acid molecules are present. In general, the work shows that there is a decided, if not very far-reaching, analogy between periodic acid and the periodates on the one hand and telluric acid and the tellurates on the other. J. F. S.

Flame Reactions of Selenium and Tellurium. Harry B. Weiser and Allen Garrison (*J. Physical Chem.*, 1919, **23**, 478—497. Compare A., 1914, ii, 317, 398; also Papish, this vol., ii, 105).—The luminescence and the nature of the deposits produced when selenium and tellurium are introduced into various flames have been experimentally examined. The flames used were: air–hydrogen, bunsen, hydrogen–air, and chlorine–hydrogen; the effect of cathode rays on sulphur, selenium, and tellurium was also examined. It is shown that the reaction from selenium to selenic salt produces a blue luminescence, which is the most characteristic in flames containing selenium. It is probable that this luminescence is due chiefly to the reaction from selenic ion to unionised selenic salt. The reaction from tellurium to tellurous salt produces a green luminescence; and from tellurous salt to telluric salt a blue luminescence. It is probable that the green luminescence is due chiefly to the reaction from tellurous ion to the unionised tellurous salt; and the blue luminescence from telluric ion to the undissociated telluric salt. Under certain conditions a red luminescence occurs in flames containing selenium, which is, as a rule, less intense than the blue luminescence. Since the vapours of both elements are coloured, it is probable that the red coloration in both cases is due in part to the colour of the vapours, in part to a purely thermal luminescence, and in part to some stage of the chemical reaction from the vapour of the element to the quadrivalent ion. A green

tip in the flames in air charged with selenium and tellurium compounds is not a luminescence, but is due to the green colour of the vapour of the dioxide, which appears greener by reflecting the blue luminescence just below. J. F. S.

The Determination of the Rate of Solution of Atmospheric Nitrogen and Oxygen by Water. II. W. E. Adeney and H. G. Becker (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 609—628).—The work previously recorded (compare this vol., ii, 104) has been continued with the object of reducing the observations to unit area and volume, and has been extended to include oxygen and nitrogen as pure gases. The apparatus used has also been modified so as to obtain a better temperature control and to eliminate any errors arising from the temperature and vapour pressure of the replenishing gas. A formula is given in each case for oxygen, nitrogen, and air, from which it is possible to calculate the rate of solution of the gas dealt with for any conditions of area exposed, depth, or degree of saturation, provided that the water is kept uniformly mixed. W. G.

Triatomic Nitrogen, N_3. Max Trautz (*Zeitsch. Elektrochem.*, 1919, **25**, 297—300).—A mathematical paper, in which it is shown that at all temperatures above that of liquid air the predominating constituent of active nitrogen (Strutt, T., 1918, **113**, 200) is triatomic nitrogen, N_3. The concentration of this substance in active nitrogen is represented by its partial pressure, 0·002 mm. The heat of formation from N_2 and N has a maximum value of 5000—10,000 cal. It is therefore, at ordinary temperatures, so much more stable than a mixture of N_2 and N that the decomposition $N_3 + N = 2N_2$ increases because of the relatively large increase in the concentration of triatomic nitrogen with falling temperature. In this fact the irregular temperature-coefficient finds its meaning. Since the cooling of active nitrogen by liquid air does not occur instantaneously, the triatomic nitrogen and the trimolecular destruction of active nitrogen, at temperatures above that of liquid air, predominate over the monatomic nitrogen and its binary compound N_2. The velocity constant of the third order is of the dimension 10^{17} mol./c.c. as a maximum, and can be much smaller if the third order reaction predominates only at ordinary temperatures. The deactivating of active nitrogen with falling temperature may either pass through a minimum or it may reach a maximum, $k/K = 10^{36}$, which is in keeping with the very large inverse of the temperature-coefficient. Where the triatomic nitrogen preponderates over the monatomic nitrogen at low temperatures above that of liquid air, hexatomic nitrogen must of necessity be formed in the mixture, in quantities which are very small compared with the triatomic nitrogen. The small heat of formation of triatomic nitrogen which is deducible from the very large reaction velocity and is in keeping with the ineffectual attempts to prepare it pure, indicates that it is impossible to prepare this substance pure by thermal methods alone. For on cooling it reacts with monatomic nitrogen to form diatomic nitrogen, and on warm-

ing it decomposes into monatomic nitrogen and hexatomic nitrogen. It is extremely probable that triatomic nitrogen is an open-chain molecule, and that similar triatomic molecules of oxygen, chlorine, bromine, and iodine can also exist, whilst a similar hydrogen molecule cannot exist. The open-chain structure for triatomic nitrogen is indicated by the nitride formation and by the absence of azide formation. The triatomic oxygen will be an isomeride of ozone.

J. F. S.

The Discovery of Phosphorus Two Hundred and Fifty Years Ago. Hermann Peters (*Prometheus*, 1919, **30**, 249—251, 259—261; from *Chem. Zentr.*, 1919, iii, 111).—Evidence is adduced to show that Hennig Brand is the sole discoverer of phosphorus, and that the rapid spread of the knowledge of the method of preparation is due to Leibniz. The discovery was made in 1669. The application of phosphorus to technical purposes was hindered at first by its high price. The latter was greatly reduced about a hundred years later, when phosphorus was extracted from bone ash by P. Gahn and Scheele. The first phosphorus matches, the so-called Turin candles, were introduced into commerce at the end of the eighteenth century. At the beginning of the nineteenth century the first phosphorus–sulphur matches were made on a small scale, but the actual production of phosphorus matches dates from about 1833. Johann Kunckel's claim of the independent discovery of phosphorus is unfounded, and was disputed by Leibniz. H. W.

Separation by Solidification of Pure Carbon Dioxide from a Gaseous Mixture. V. Crémieu and A. Lepape (*Compt. rend.*, 1919, **169**, 654—655).—Carbon dioxide may be obtained in a pure, solid state from a gaseous mixture rich in that gas either by allowing the compressed gas to expand suddenly from a narrow orifice through a cloth bag into the air or by compressing the mixture slightly in a vessel cooled to $-80°$. The solid carbon dioxide is, in either case, free from radium emanation when the latter is present in the original mixture. W. G.

The Effect of Sea-salt on the Pressure of Carbon Dioxide and Alkalinity of Natural Waters. Edmund Brydges Rudhall Prideaux (T., 1919, **115**, 1223—1230).

The Solubility of the Inert Gases in Liquids. Andreas von Antropoff (*Zeitsch. Elektrochem.*, 1919, **25**, 269—297).—The solubility of helium, argon, neon, krypton, and xenon has been determined in water at various temperatures, and the solubility of krypton has been determined in pentane, acetic acid, and aniline. Several pieces of apparatus are described which are specially designed for working with the inactive gases. These include (1) a simplified and improved form of the Toepler mercury pump; (2) an absorption pipette, which enables an absorbing liquid or solution to be introduced into a gas contained over mercury, and to be withdrawn again without loss of gas; (3) an apparatus for solubility deter-

minations, in which neither the liquid nor its vapour comes into contact with taps, and (4) a burette in which the gas can be expelled from solution, and which allows of a definite amount of liquid being introduced into the solubility apparatus. The original should be consulted for details and dimensions of the apparatus. The helium used in the experiments was obtained by heating clevite at 1000° in a porcelain tube, and the product purified in the usual way. The following solubilities (β) in water were obtained: 0°, 0·00967; 10°, 0·00991; 20°, 0·00996; 30°, 0·01007; 40°, 0·01029; 50°, 0·0108. These figures are about 40% smaller than the values found by Estreicher (A., 1900, ii, 205). Argon, krypton, and xenon were separated by a method similar to that of Ramsay and Moore (T., 1908, **93**, 2181). The following solubility values in water were obtained: Neon, 0°, 0·0114; 10°, 0·0118; 20°, 0·0147; 30°, 0·0155; 40°, 0·0217; 50°, 0·0322. Krypton, 0°, 0·1095; 10°, 0·0807; 20°, 0·0626; 30°, 0·0511; 40°, 0·0433; 50°, 0·0383; 60°, 0·0357. Xenon, 0°, 0·2200; 10°, 0·1580; 20°, 0·1109; 30°, 0·0893; 40°, 0·0745; 45·45°, 0·0663. In pentane, xenon has the following absorption coefficients: 11·7°, 0·1686; 20°, 0·1335; 25°, 0·1272; 30°, 0·1009; 40°, 0·0949; 49·5°, 0·1084; in aniline, the solubilities per gram are: 10°, 0·6687; 20°, 0·5006; 30°, 0·4426; 40°, 0·4336; 50°, 0·3892. The solubility of the inert gases in water increases with the molecular weight, and in the case of the heavier gases, niton, xenon, krypton, and argon, decreases with increasing temperature. The solubility of helium is practically independent of temperature, whilst that of neon increases rapidly with increasing temperature.

J. F. S.

Solubility of Calcite in Sea-water in Contact with the Atmosphere and its Variation with Temperature. Roger C. Wells (*Carnegie Inst. Publication*, 1918, No. 213 [*Papers from Dept. Marine Biology*, **9**, 316—318).—Certain equilibria, the attainment of which would be expected from experiments in the laboratory, do not seem to be fully attained under natural conditions in the ocean. The equilibria referred to involve the effect of temperature on the exchange of carbon dioxide between sea-water and the atmosphere and the precipitation or solution, as the case may be, of various solid constituents from or into sea-water. Apparently the adjustments occur so slowly, and the bulk of the ocean is so great, with reference to the surface exposed to the atmosphere, that the expected variations with temperature do not appear in the water of the open ocean. Sea-water in contact with an excess of calcite was agitated by a current of outdoor air for forty days, and the dissolved carbonates were estimated at intervals by titration with 0·02*N*-sodium hydrogen sulphate, using methyl-orange as an indicator. Experiments were made at 1° and at the ordinary temperature (25° to 29°). The colder sea-water tended to retain more carbonate in solution than warmer sea-water, but did not dissolve fresh calcite. Ordinary sea-water appears to contain so much carbonate that in contact with the atmosphere at 1° it

neither has nor acquires an appreciable solvent action on calcite. At higher temperatures, it undergoes a slow diminution in its content of carbonates on being agitated in contact with outdoor air.

CHEMICAL ABSTRACTS.

Gravitational Attraction and Uranium-Lead. ANDERS BULL (*Science*, 1919, **50**, 69—70).—No one has satisfactorily explained the discrepancies between the atomic weight of ordinary lead and that of lead from uranium minerals. It is suggested that a difference may exist in their behaviour towards the force of gravitation. Deviations in the value of gravitational acceleration might be proportional to variations in their atomic weight, which would make the atomic mass of all kinds of lead identical. Assuming, finally, that the gravitational attraction is due to electrons, variations in atomic weight might be ascribed to electronic tension set up in the atom by radioactive disintegration and gradually diminishing in the end-product of the series.

CHEMICAL ABSTRACTS.

Critical Study of the Potassium and Sodium Double Salts of Lead Tetrafluoride as Sources of Fluorine. GEORGE L. CLARK (*J. Amer. Chem. Soc.*, 1919, **41**, 1477—1491).—An investigation of the methods of preparation and properties of the double salts formed by lead tetrafluoride with sodium and potassium fluoride respectively, with the object of finding a suitable substance for the preparation of fluorine. *Tripotassium lead hydrogen octafluoride*, $3KF,HF,PbF_4$, is prepared by adding potassium plumbate in small quantities to a concentrated aqueous solution of hydrofluoric acid until a separation of lead dioxide occurs. The solution is filtered through paper supported by several layers of cloth, and the filtrate evaporated slowly in lead dishes on a sand-bath in a gentle current of air until a separation of crystals occurs. The solubility of this salt has been determined in the presence of hydrofluoric acid and potassium fluoride. In the absence of acid, hydrolysis occurs, with the separation of lead dioxide. When heated at 250°, the hydrogen fluoride molecule is expelled, and at temperatures above 250° fluorine is driven off. *Potassium plumbate*, $K_2PbO_3,3H_2O$, is best prepared by mixing three molecules of potassium hydroxide with 20% of its weight of water, raising the temperature to 100°, and adding one molecule of lead dioxide; action at once occurs, and the plumbate is formed without decomposition products. This salt is regarded as the dipotassium salt of orthoplumbic acid, $K_2Pb(OH)_6$, and, on treatment with water, hydrolyses according to the equations

$$K_2Pb(OH)_6 + 2H_2O \rightleftarrows 2KOH + H_2Pb(OH)_6,$$

$H_2Pb(OH)_6 = H_4PbO_4 + 2H_2O$. In the presence of 20% of water, the hydrolysis proceeds so far that hydrated lead dioxide is precipitated. *Disodium lead hexafluoride*, $2NaF,PbF_4$, is prepared by the addition of sodium plumbate to aqueous hydrofluoric acid, and crystallisation of the product from hydrofluoric acid to separate sodium hydrogen fluoride. The crystals occur in stout, short plates

which are hydrolysed by water. The solubility has been determined in water containing hydrofluoric acid and sodium fluoride, and is shown to decrease with increasing concentration of hydrogen fluoride until sodium hydrogen fluoride is formed, and then it increases in solubility with an increase in the concentration of hydrogen fluoride. This salt liberates fluorine at 250°. *Sodium plumbate*, $Na_2PbO_3,6H_2O$, is prepared by mixing 150 grams of sodium hydroxide with 50 c.c. of water at 100°, adding lead dioxide until a paste is formed, then adding 25 c.c. of water and lead dioxide to make a total quantity of 300 grams of the latter substance. This salt is much less stable and more easily hydrolysed than the potassium salt. The analysis of the double fluorides is effected in the following manner. The salt is dissolved in water, when hydrolysis occurs, thus: $2(3KF,HF,PbF_4)+4H_2O=6KF+10HF+2PbO_2$; the lead dioxide is filtered off in an alundum crucible, dried at 105°, and weighed. The filtrate is made up to a known volume; in one portion, the free acid is estimated by titration, and in another the potassium fluoride is estimated by evaporation to dryness and ignition at 500°. The two double fluorides are considered as sources of fluorine. The potassium salt is more easily prepared and is more stable than the sodium salt, and, weight for weight of materials used, the potassium salt is twice as efficient as the sodium salt. J. F. S.

Colloidal Tricalcium Aluminate. A. J. Phillips (*J. Amer. Ceram. Soc.*, 1919, **2**, 708—742).—Pure amorphous, calcined, and finely ground tricalcium aluminate forms a true colloidal sol in water, an insignificant proportion of the substance entering into true solution. The crystalline form appears to be highly polymerised, and in contact with water behaves like a colloid, but if suspension is incomplete, the residue may consist of hydrated crystals. A more concentrated suspension is obtained by using lime-water instead of pure water, and the product does not diffuse or dialyse, shows the Tyndall cone, is positively charged, is not coagulated by heat, but is coagulated by freezing, has a high adsorptive power, and generally resembles the well-known sols of ferric, aluminium, and chromic oxides. It does not form a gel on evaporation or by dehydration over sulphuric acid, the product in each case being a loose powder. The lime:alumina ratio in the filtered suspensions never corresponded with $3CaO,Al_2O_3$, lime always being deficient, but to an irregular extent, varying with the time, from 1:1·096 after three hours to 1:1·519 after twenty-eight days. The deficiency in the lime is attributed to the free lime being adsorbed by the colloidal aluminate.

The colloidal aluminate is an anhydride which, by capillary attraction, endosmose and molecular imbibition, swells, forming an emulsoid. On the first addition of water to the aluminate, there is a development of heat—due to the formation of an exothermic hydrate. The aluminate is more soluble in cold than in hot water, so that if it is first exposed to moist air and then mixed with water, the conditions favour a great concentration of aluminate in true

solution, this being accompanied by an endothermic change. There is a further development of heat resulting from the disturbance of the equilibrium $(H_2O)_n \rightleftharpoons nH_2O$ of the water-molecules. This is also eliminated when the aluminate has previously been exposed to moist air. When there is a sufficient concentration of cations to disperse the hydrated aluminate as fast as it is formed, the resultant heat effects are either zero or negative, as this dispersion is accompanied by an absorption of heat. The treatment of the colloidal gel only changes the composition of the outer surface; any ionic activity is confined to the surface, except when the film is ruptured, and is a characteristic adsorption effect.

A greater dispersion of aluminate occurs in lime-water than in pure water, as the calcium ions of the calcium hydrate are adsorbed more than the hydroxyl ions by the hydrated aluminate, and when a sufficient number of ions has been adsorbed, their charges and those of the aluminate repel each other, and the aluminate is thereby dispersed.

Any water adsorbed is compressed in the process, any salts in solution being similarly compressed, and their solubility is increased.

As the aluminate can only adsorb a limited amount of cations, when the concentration of the anions is sufficiently increased, the positive charges on the aluminate will be neutralised by the adsorption of the anions because of their increased concentration, and uncharged aluminate is precipitated. The adsorbing surface is decreased, and the ions previously held by adsorption are returned to the solution and exercise a dispersive effect on undispersed material. Hence the concentration of negative ions is greatly increased. A much weaker solution of sodium hydroxide shows the same precipitating effect.

When a smaller amount of water is used, as in preparing cement pastes, the aluminate is converted into a colloidal gel which persists for at least twenty-four hours. On continuing the mixing of the aluminate and water for several minutes, a considerable retardation occurred in the time of setting, but by increasing the percentage of hydrate, so that the total ion-concentration exceeded the adsorptive capacity of the aluminate for cations, the time of setting was reduced. A semipermeable film is formed around the grains of aluminate, which is destroyed on mechanical agitation, a sol being formed at the same time.

On stirring a mixture of equal weights of the aluminate and water, and then slowly adding a volume of hydrochloric acid (D 1·21) equal to that of the water, continuing the stirring and keeping the vessel cool, the viscous paste soon solidifies, and, on keeping, synoresis occurs, an aqueous layer separates, and solidifies to a clear gel containing both alumina and lime.

The rate of coagulation of the aluminate gel is thus affected by the amount of dispersion effected, the synoresis of the gel, the neutralisation of previously adsorbed calcium ions by hydroxyl ions, and the adsorption of undissociated salt. [See also *J. Soc. Chem. Ind.*, 1919, 904A.] A. B. S.

Rôle of Water of Crystallisation and the Structure of Alums. CLEMENS SCHAEFER and MARTHA SCHUBERT (*Ann. Physik*, 1919, [iv], **59**, 583—588).—Polemical. It is shown that the crystal model of alum put forward by Vegard and Schjelderup is not correct (A., 1918, ii, 156). It is maintained that the rôle allotted to the water of crystallisation in the crystalline structure of alums by Vegard was put forward by the present authors two years previously (A., 1916, ii, 505). The authors therefore claim priority in this matter. J. F. S.

Amalgams. II. Colloidal Gold Amalgam. C. PAAL and HERMANN STEYER (*Kolloid Zeitsch.*, 1919, **25**, 21—26. Compare this vol., ii, 69).—The gold amalgam sol previously described, on keeping, is oxidised to some extent by atmospheric air; this partly oxidised sol has a somewhat browner solution than the sol when freshly prepared, but may be brought back to its original colour by the addition of a few drops of hydrazine hydrate solution. A small quantity of the sol was kept in solution for twenty-two weeks with the object of determining its stability. It was found that the colour became more fiery-red and that a heavy, grey gel separated. The remaining solid was dried in a vacuum and gave a blackish-violet substance, which was in the form of lamellæ with a bronze tinge; it was completely soluble in water, and had the composition $AuHg_{0\cdot34}$. The gel contained 5·32% of lysalbic acid, which was used as a protecting colloid, and had the composition $AuHg_{0\cdot9}$. The gel was non-reversible on warming with either sodium hydroxide or ammonia solution. A number of other experiments are described on the stability of the colloid. J. F. S.

Mineralogical Chemistry.

A Lead-grey, Fibrous Mineral from Binn, Switzerland. R. H. SOLLY. With a chemical analysis by G. T. PRIOR (*Min. Mag.*, 1919, **18**, 360—362).—Fine, acicular crystals associated with seligmannite, and sometimes grouped as triangular lattices in cavities of the dolomite, resemble in their cleavage, colour, and chocolate-coloured streak the several thioarsenites of lead (liveingite, rathite, baumhauerite, and dufrenoysite) found at this locality. Goniometric measurements in the prism-zone, the only one developed, accord more closely with the angles of dufrenoysite, whilst the analysis corresponds with rathite, $3PbS,2Sb_2S_3$. The presence of thallium is of interest (compare A., 1918, ii, 323).

Pb.	Ag.	Cu.	Tl.	Fe.	As.	Sb.	S.	Insol.	Total	D_4^{15}.
51·11	0·76	0·10	0·23	0·21	23·37	0·74	23·22	0·24	99·98	5·453

L. J. S.

Semseyite from Dumfriesshire. G. F. Herbert Smith. With a chemical analysis by G. T. Prior (*Min. Mag.*, 1919, **18**, 354—359).—Specimens of ore from the old antimony–lead mine at Glendinning in Eskdale show small cavities with a drusy lining of minute, iron-black crystals of a thioantimonite of lead. The associated minerals are stibnite, valentinite, ankerite, calcite, blende, and pyrites. The crystals are monoclinic with constants ($a:b:c=1{\cdot}1356:1:1{\cdot}0218$, $\beta=74°14'$) somewhat different from those previously determined for plagionite and semseyite; but the following analysis of the drusy lining, together with the underlying massive material, agree with the semseyite formula, $9PbS,4Sb_2S_3$.

Pb.	Sb.	S.	Fe.	Zn.	$CaCO_3$.	$MgCO_3$.	Insol.	Total.	Sp. gr.
52·37	25·49	18·81	0·67	trace	1·66	trace	0·81	99·81	5·84

L. J. S.

Ferrazite, a New Associate of the Diamond. T. H. Lee and Luiz Flores de Moraes (*Amer. J. Sci.*, 1919, [iv], **48**, 353—354).—Some dark yellowish-white pebbles ("favas") from the Brazilian diamond deposits gave the following results on analysis. After deducting silica and alumina as kaolinite and wavellite, the formula is $3(Pb,Ba)O,P_2O_5,8H_2O$. Thin sections under the microscope show a granular structure, D 3·0—3·3:

PbO.	BaO.	CaO.	Al_2O_3.	P_2O_5.	SiO_2.	H_2O.	Total.
45·63	8·87	trace	3·48	26·24	2·44	14·20	100·86

L. J. S.

Crystallography of Vogtite, an Anorthic Metasilicate of Iron, Calcium, Manganese, and Magnesium, from Acid Steel-furnace Slags. A. F. Hallimond (*Min. Mag.*, 1919, **18**, 368—372).—Acid steel-furnace slags consisting mainly of FeO, MnO, and SiO_2 yield the silicates fayalite and rhodonite; but when the amount of lime exceeds about 8% the new silicate *vogtite* separates as long, blade-like crystals. The composition of these is given under I, agreeing approximately with $(Fe,Ca,Mn,Mg)SiO_3$; II gives the composition of the slag. The crystals are anorthic, $a:b:c=1{\cdot}093:1:0{\cdot}729$, $\alpha=99°37'$, $\beta=99°21'$, $\gamma=83°53'$, with perfect cleavages parallel to $M(\bar{1}10)$ and $m(110)$. Optical determinations are given; $\beta=1{\cdot}701$, $2V_D=65\frac{1}{2}°$, optically negative. The crystals, when free from included glass, are transparent and pale amber-yellow in colour:

	SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	CaO.	MgO.	TiO_2.	Total.	Sp.gr.
I.....	47·4	0·15	2·7	15·95	12·95	15·1	5·26	0·10	99·61	3·39
II.....	47·9	1·72	1·2	20·85	10·8	13·0	3·89	0·58	99·4	—

Vogtite differs in density and optical orientation from pyroxmangite (A., 1913, ii, 869) and sobralite (this vol., ii, 165). L. J. S.

The Rôle of Boron in Silicates. G. Cesaro (*Riv. Min. Crist., Ital.*, 1918, **50**, 3—31).—The compositions of borosilicate minerals are discussed, and it is shown that in every case the function of boron is best explained as that of an acid. Datolite is accordingly

an acid metasilicate of calcium, with some silicon replaced by "(B_2O)." Homilite is similar, containing also iron. Euclase corresponds with datolite with aluminium instead of boron, and glucinum instead of calcium. A table is given showing the existence in minerals of acids of boron corresponding with each of those of silicon. Axinite is a combination of di-ortho- and meta-silicates, or a basic triple metasilicate, with B_2O replacements. Tourmaline is an orthosilicate with part of the silicon replaced by B_2O. Danburite is a neutral tricalcium metasilicoborate. Howlite is an orthosilicate, with replacement. In addition to these, the natural borates can be expressed by structural formulæ. The possible constituents of boron acids are discussed. CHEMICAL ABSTRACTS.

Analytical Chemistry.

Tincture of Muscari as an Indicator. E. DUFILHO (*Bull. Soc. Pharm., Bordeaux*, 1918, **4**, 202; from *Ann. Chim. anal.*, 1919, [ii], **1**, 325—326).—An alcoholic extract of muscari flowers (grape-hyacinth) may be used as an indicator in acidimetry, the colour change being from red in acid solution to green in alkaline solution. It behaves like litmus in the case of mineral acids, oxalic acid, alkalis and ammonia, and like methyl-orange with phosphoric acid; it is not affected by boric acid except in the presence of glycerol.
W. P. S.

Coloured Indicator Papers. I. M. KOLTHOFF (*Pharm. Weekblad*, 1919, **56**, 175—187).—An examination of the sensitiveness of indicator papers with reference to the quality of the paper itself and its pre-treatment with acid, alkali, or aluminium hydroxide; the nature of the colouring matter used, and its concentration on the paper. Sized papers are less sensitive than unsized, although the reaction on the former is sharper. Otherwise the kind of paper used, and any previous treatment it may have had, are of little importance. The most sensitive Congo paper was obtained by treating filter paper with a 0·1% solution of the dye. This indicated an acidity of 0·0001*N*-hydrochloric acid. The most sensitive paper for strong acids and bases is prepared from a 0·1% solution of azolitmin.
W. S. M.

Titration of Acids by the Conductivity Method. P. A. MEERBURG (*Chem. Weekblad*, 1919, **16**, 1338—1347).—In the titration of various acids with alkalis the author has determined the neutralisation point by a conductivity method. If a graph is plotted in which the abscissæ are represented by c.c. of 0·86*N*-sodium

hydroxide and the ordinates by the values $(1000-a)/a$, the neutralisation point will be indicated by a definite bend in the curve. With a strong acid and base this bend will be sharp, but it will be obtuse in the case of a weak acid and strong base. With acids and bases having a dissociation-constant, $K>10^{-10}$, the neutralisation point is readily determined (Dutoit and Duboux, "L'analyse des vins par volumétrie physico-chimique," 54), but if hydrolysable salts are formed the curve becomes continuous and the neutralisation point is masked. In titrating a mixture of two acids having widely differing degrees of ionisation, for example, hydrochloric acid and phenol, the neutralisation of the hydrochloric acid takes place first and is indicated by the lowest portion of the curve, a sharp bend then denoting the neutralisation of the phenol. When the acids have the same ionising power, the method fails, as the lowest point on the curve cannot be accurately determined. Accurate results are obtainable in cases where the relative proportions of the stronger acid to the weaker are 1 : 1 or 1 : 2·5, but when the proportions were 2·5 : 1 the author found the results too low for the strong acid and too high for the weaker one. Tables and curves are given for various acids, such as hydrochloric acid, oxalic acid, lactic acid, and mixtures of these. The method is suitable for the estimation of small amounts of acidity, as, for example, in chyle. W. J. W.

The Amalgamated Copper Cathode in Electro-analysis. José Alemany y Selfa (*Anal. Fis. Quim.*, 1919, **17**, 174—188).—The advantages in the use of mercury as cathode material in the electrolytic precipitation of metals are neutralised to some extent by the difficulties of manipulation. These difficulties are obviated by the use of the amalgamated electrode described. The cathode is of copper gauze, 5·5 × 11 cm. On this is deposited about 1 gram of silver by electrolysis in alkaline silver cyanide solution. The cathode is then amalgamated by electrolysis in mercurous nitrate solution until 0·8—1·5 gram of mercury has been deposited. It is then washed with water, alcohol, and ether. In combination with this cathode a rotating anode of platinum or of iron is employed. The temperature of electrolysis must not exceed 45°. A detailed account of the following electrolytic estimations is given: zinc in alkaline, ammoniacal, and neutral solution in presence of nitrate; zinc in sulphuric acid solution; cadmium in ammoniacal solution in presence of nitrate; cadmium in sulphuric acid and in neutral solution. In all cases the results obtained were excellent. W. S. M.

Graphic Representation of the Chemical Composition of Natural Waters. Enrique Herrero Ducloux (*Anal. Fis. Quim.*, 1917, **15**, 477—483).—The analytical results are graphically represented in relation to a regular hexagon of reference. The amounts of the six commonly occurring cations, Fe''', Al''', Ca'', Mg'', K', Na', are measured off in an invariable order along the six axes radiating from the centre of the hexagon through the vertices and the points thus marked off are joined. The six anions, SiO_3'', SO_4'', HCO_3', Cl', NO_3', HS', are similarly treated. The chemical

composition of the water is completely represented by the two irregular hexagonal figures so formed. W. S. M.

Chemical Analysis with Membrane Filters. Richard Zsigmondy and Gerhart Jander (*Zeitsch. anal. Chim.*, 1919, **58**, 241—280).—The membrane filters described by Zsigmondy and Bachmann (A., 1918, ii, 307) may be used generally in analysis; the filtration is rapid, the precipitate is washed readily, and very fine crystalline or colloidal precipitates are retained completely by the filters. The membrane is mounted for use in the apparatus (flanged funnel, perforated disc and ring) described previously by Zsigmondy (A., 1913, ii, 857). W. P. S.

Estimation of Small Quantities of Alkali Iodides in the Presence of Bromides and Nitrites. Ed. Lasausse (*J. Pharm. Chim.*, 1919, [vii], **20**, 177—181).—The nitrite is oxidised by potassium permanganate in phosphoric acid solution at 40°; sodium hydrogen sulphite is then added to reduce chlorates and bromates, and the solution is boiled with the addition of potassium hydroxide and potassium permanganate; the iodide is thus converted into iodate, whilst the chloride and bromide are not affected. The iodate is then determined iodometrically. [See, further, *J. Soc. Chem. Ind.*, 1919, 899A.] W. P. S.

Estimation of Iodine in Cuprous Iodide. Ed. Lasausse (*J. Pharm. Chim.*, 1919, [vii], **20**, 181—183).—Two methods are described. In the first, the cuprous iodide is decomposed with ferric chloride solution, the liberated iodine dissolved in carbon disulphide, and the solution separated and titrated. In the second method, the cuprous iodide is boiled with potassium hydroxide solution, and the resulting potassium iodide estimated in the solution by oxidation to iodate by means of potassium permanganate in alkaline solution, as described in the preceding abstract. [See, further, *J. Soc. Chem. Ind.*, 1919, 899A.] W. P. S.

Modified Benedict Method for the Estimation of Sulphur in Feeds, Fæces, and Foods. J. O. Halverson (*J. Amer. Chem. Soc.*, 1919, **41**, 1494—1503).—The following modified Benedict method for the estimation of sulphur in foods and fæces is described. About 3·44 grams of fæces or 2·7476 grams of cattle food are rolled up in half a filter paper and placed in a 300 c.c. Kjeldahl flask. Ten to fifteen c.c. of hot water are added, and the flask heated on a steam-bath with slight shaking, 20 c.c. of a mixture of concentrated and fuming nitric acid (1:4) are added, the flask stoppered with a small funnel, and kept for twelve hours. It is then placed on a steam-bath and digested for four days with occasional shaking. At the end of that time, a further 10 c.c. of the acid mixture are added, and the digestion continued until the solution is clear, when it is transferred in portions to a 60 c.c. evaporating basin and treated with 20 c.c. of the Benedict reagent during evaporation to complete dryness on the steam-bath. It is

then slowly baked on a sand-bath. The blackened residue is heated until it fuses, and then the temperature is lowered so that it solidifies slowly. About 20 c.c. of (1:4) hydrochloric acid are added, and the mixture heated for fifteen minutes on the steam-bath. The clear solution is then filtered into a 250 c.c. beaker, made up to 100 c.c. with water, heated to boiling, and treated with 10 c.c. of boiling 5% barium chloride solution from a dropper; the addition should take four minutes. The precipitate is digested for two to three hours on a hot plate, and then kept cold for forty-eight hours and filtered. It is shown that when silica is present, the peroxide method has a tendency to give high results. When the silica is removed, the results agree with those of the Benedict method to the third decimal place. J. F. S.

Gravimetric Estimation of Sulphate as Barium Sulphate. I. M. KOLTHOFF and E. H. VOGELENZANG (*Pharm. Weekblad*, 1919, **56**, 122—142).—A detailed investigation into the sources of error in the estimation of sulphate as barium sulphate. The solubility of barium sulphate is increased by the addition of acids or of salts, except in the case where barium ion or sulphate ion is supplied. Samples of barium sulphate prepared in various ways show differences in solubility depending chiefly on the size of the particles. The solubility in water at ordinary temperatures is negligible. The solubility figures obtained in hydrochloric acid solution for acid concentrations $N/1$, $N/2$, $N/10$ are, respectively, 54, 31, and 11 mg. per litre. At 90°, the solubilities in $N/1$-, $N/2$-, and $N/20$-acid were 416, 265, and 77 mg. per litre respectively.

In the estimation, reduction of barium sulphate during ignition of the dry precipitate and filter was found to take place to a slight extent in a porcelain crucible, and to a considerable extent in platinum. This can be avoided by ignition of the moist filter. Simultaneous precipitation of other salts with barium sulphate is caused by: (1) "conglomerate formation"; (2) solid solution; (3) adsorption; (4) mixed crystals; (5) mechanical inclusion; (6) chemical reaction. With regard to (2) and (3), experiments showed that in acid solution barium sulphate did not absorb electrolytes; (4) is an improbable case, as the commonly occurring salts in the precipitation belong to a different crystallographic group. Impurities in the barium sulphate are accounted for chiefly by the reactions between the SO_4'' ion and the intermediate ions of other salts (ternary electrolytes) present. Excess of barium chloride, for example, gives rise to the formation of $BaCl^{\cdot}$, which reacts thus: $SO_4'' + 2BaCl^{\cdot} = Ba_2Cl_2SO_4$. The error in this case is in excess. Potassium sulphate gives KSO_4', which with $Ba^{\cdot\cdot}$ gives $2KSO_4' + Ba^{\cdot\cdot} = BaK_2(SO_4)_2$, giving an error in defect (Richards and Parker, A., 1895, ii, 370). The occlusion of barium chloride can be avoided to some extent by precipitation in dilute solutions and at as high a temperature as possible, conditions unfavourable to the formation of complex ions. The assertion of Allen and Johnston (A., 1910, ii, 650) that $Ba_2Cl_2SO_4$ can be freed from

chlorine by ignition could not be confirmed, as the presence of chloride was proved in all cases after fusion of the precipitate with carbonate. Similarly, the statement of Pregl ("Die quantitative organische Mikroanalyse," 1917, p. 29) that occluded barium chloride can be washed out after ignition of the precipitate, could not be confirmed. The authors recommend results to be corrected for the presence of chloride by fusion of the precipitate with sodium carbonate and estimation of the chlorine. The presence of nitrate gives rise to a greater error than chloride. Errors due to the occlusion of calcium, iron, and potassium are chiefly to be ascribed to the formation of complex ions. Phosphate is precipitated as barium phosphate along with the sulphate. The authors are of opinion that it is impossible to give general directions for the accurate estimation of sulphate in solutions. W. S. M.

Estimation of Sulphate as Strontium Sulphate. I. M. Kolthoff and E. H. Vogelenzang (*Pharm. Weekblad*, 1919, **56**, 159—161).—Following on their work on the precipitation of sulphates as barium sulphate (see preceding abstract), the authors have investigated the estimation of sulphate as strontium sulphate. Preliminary solubility determinations showed that strontium sulphate is practically insoluble in 50% ethyl alcohol. The sulphate is precipitated in the cold by 10% strontium chloride solution. An equal volume of 96% ethyl alcohol is added, and, after settling at the ordinary temperature, the precipitate is collected and washed with 50% alcohol. The moist filter is burned and ignited. Estimations were carried out in neutral solutions and in presence of hydrochloric acid, sodium acetate, ammonium chloride and nitrate, potassium chloride, sodium chloride and nitrate. Considerable errors in defect were observed. To eliminate the simultaneous precipitation of iron salts, sugar, glycerol, lactic and oxalic acids were added. These rendered filtration difficult without improving the results. The authors conclude that, in general, accurate results are not to be expected from this method. W. S. M.

Modifications of Pearce's Method for Arsenic. John Waddell (*J. Ind. Eng. Chem.*, 1919, **11**, 939—941).—The following alterations are made in Bennett's and Canby's modifications of Pearce's method (A., 1899, ii, 519) in order to render them trustworthy. In Bennett's method, nitric acid should be added to neutralise any large excess of alkali in the solution, the latter then rendered slightly alkaline with sodium hydroxide, and acidified very slightly with acetic acid before the arsenic is precipitated as silver arsenate. Canby's method is modified in a similar way, except that in place of acetic acid, nitric acid is added in slight excess, and, after the addition of silver nitrate, this excess is neutralised by zinc oxide. W. P. S.

Reaction between Arsenious Oxide and Iodine. I. M. Kolthoff (*Pharm. Weekblad*, 1919, **56**, 621—634).—The reaction $As_2O_3 + 2I_2 + 2H_2O \rightleftharpoons As_2O_5 + 4HI$ is studied with reference to the

limits of hydrogen-ion concentration within which a definite end-point is obtained. The hydrogen-ion concentration is determined colorimetrically by means of various indicators. In the titration of $N/10$- and $N/100$-arsenious oxide solutions with iodine, the final acidity must lie between $10^{-11\cdot0}$ and $10^{-5\cdot0}$ mol. hydrogen ion per litre. In the titration of $N/10$- and $N/100$-iodine solutions with arsenious oxide solution, the initial limits are $10^{-9\cdot0}$ and $10^{-5\cdot5}$, and the final $10^{-8\cdot0}$ and $10^{-5\cdot0}$. The purity of the arsenious oxide used is best estimated by measurement of the conductivity of a saturated solution. The commonly occurring impurity is arsenic oxide, which may be estimated by means of the reaction of the solution with dimethyl-yellow and methyl-red. Neutral or weakly acid solutions of arsenious oxide are stable, and may be kept indefinitely without change of titre. In alkaline solutions, oxidation of arsenious to arsenic oxide takes place. W. S. M.

Method for Estimation of Carbon by Wet Combustion, using Barium Hydroxide as Absorbent. P. L. Hibbard (*J. Ind. Eng. Chem.*, 1919, **11**, 941—943).—A convenient method of procedure and apparatus for use in the method are described. The substance is oxidised by heating in a flask with chromic acid and sulphuric acid, and the resulting carbon dioxide is carried by a current of air into an excess of standard barium hydroxide solution; at the end of the operation, the excess of barium hydroxide is titrated with hydrochloric acid, using phenolphthalein as indicator. The air used is first passed through a soda-lime tube; after leaving the oxidation flask, the air carrying the carbon dioxide, etc., passes through a condensing tube, a tube filled with beads moistened with sulphuric acid, and a tube filled with amalgamated granulated zinc, before it enters the barium hydroxide solution; the latter is contained in an inclined flask, into which extends the lower end of a Meyer bulb tube. W. P. S.

Microchemical Identification of Lead. G. Denigès (*Bull. Soc. Pharm., Bordeaux*; from *J. Pharm. Chim.*, 1919, [vii], **20**, 159—160).—Soluble lead salts yield characteristic crystals of lead iodide when treated with a drop of potassium bromide solution and a drop of potassium iodide solution. With insoluble lead salts, the addition of a drop of sulphuric acid is necessary. Lead chromate, cyanide, and fluoride should be evaporated with hydrochloric acid, and metallic lead and lead sulphide with nitric acid, before the test is applied. W. P. S.

Titrimetric Estimation of Lead. Paul Holmsen (*Tidskr. Kemi Farm. Ter.*, 1919, **16**, 110—113).—A solution, not exceeding 100 c.c., containing 0·5—0·1 gram of lead, neutralised with ammonia, is acidified with 15 c.c. of acetic acid, 10 grams of ammonium acetate added, and the liquid warmed to 70—80°. The lead is precipitated by slowly adding 10 c.c. of ammonium molybdate solution, with constant stirring, warming for fifteen minutes, setting aside for thirty minutes, filtering, and washing with hot

water. The precipitate is treated with 50 c.c. of dilute sulphuric acid and hot water, 10 grams of pure zinc added, and boiled for ten minutes, filtered, washed with hot water, and the molybdenum in the filtrate titrated with 0·1*N*-permanganate. One c.c. of 0·1*N*-permanganate is equivalent to 0·007296 gram of lead.

CHEMICAL ABSTRACTS.

Microchemical Reactions with Thiosulphuric Acid. A. BOLLAND (*Compt. rend.*, 1919, **169**, 651—654).—Sodium thiosulphate gives crystalline precipitates, which are well defined when examined microscopically, with thallous nitrate, barium chloride, lead acetate, and benzidine. Sketches are given of the microcrystalline structure of these precipitates. In the case of barium chloride, the appearance of the precipitate varies with the experimental conditions. It is preferable, in this case, to use a concentrated solution of the thiosulphate. W. G.

Electroanalysis of Copper without Platinum Electrodes. JUAN GUITERAS (*Anal. Fis. Quim.*, 1919, **17**, 209—216. See A., 1915, ii, 652, and 1916, ii, 199).—A copper cathode and a rotating anode of passive iron were employed. 0·1—0·2 Gram of electrolytic copper was dissolved in twenty drops of nitric acid for each estimation, and the various electrolytes were prepared by the addition of the following solutions: (1) 5 grams of disodium phosphate in water and 15 c.c. of concentrated ammonia solution; (2) 5 c.c. of 50% ammonium acetate solution and 15 c.c. of ammonia; (3) 3 grams of ammonium oxalate in water and 15 c.c. of ammonia; (4) 15 c.c. of formic acid solution (75 c.c. of water and 25 c.c. of formic acid, D 1·2) and 15 c.c. of ammonia; (5) 2 grams of citric acid in water and 15 c.c. of ammonia; (6) 2 grams of boric acid in water and 15 c.c. of ammonia. During electrolysis, the electrolyte was kept warm and the voltage gradually reduced from about 3 volts to 1·7—1·8 volts. The experiments were repeated with the constant voltage of one accumulator throughout. In all cases, the deposits on the cathode were coherent and the results satisfactory. Experiments in ammoniacal solutions of thiocyanate gave inaccurate results. W. S. M.

New Separation of Aluminium and Vanadium. P. WENGER and H. VOGELSON (*Helv. Chim. Acta*, 1919, **2**, 550—553).—Methods are described for the quantitative separation of (1) aluminium and vanadium, (2) aluminium, iron, and vanadium. In the case of aluminium and vanadium the mixture of oxides is heated with six times its weight of anhydrous sodium carbonate, at first gradually, until the mass melts, and then at a higher temperature for three hours. The crucible and contents are allowed to cool somewhat, plunged into distilled water, and raised to the boiling point, when a clear solution of sodium aluminate and vanadate is obtained. The solution is made up to 500 c.c. with distilled water, raised to the boiling point, and treated with about ten times its weight of ammonium nitrate in small quantities. Aluminium hydroxide is pre-

cipitated, filtered, washed, ignited, and weighed as Al_2O_3. The filtrate is acidified with hydrochloric acid, neutralised with ammonia, raised to the boiling point, and treated with barium chloride solution. Barium vanadate is precipitated; the precipitate is kept for twenty-four hours, filtered, washed with cold water, dried, ignited, and weighed as $Ba(VO_3)_2$. In the presence of iron a solution is made which is precipitated cold by ammonia. This precipitate, which contains iron and aluminium hydroxides and ammonium vanadate, is filtered, washed, ignited in a platinum crucible, mixed with six times its weight of sodium carbonate, and ignited as before. The fused mass is dissolved in water to which 1 gram of sodium carbonate has been added. The iron left insoluble as oxide is filtered off and weighed, and the filtrate treated as described above. The results of the analyses are extremely good. J. F. S.

Sulphite Method for the Separation and Estimation of Gallium when Associated with Zinc. Lyman E. Porter and Philip E. Browning (*J. Amer. Chem. Soc.*, 1919, **41**, 1491—1494).—Gallium is conveniently precipitated from neutral or acid solutions of zinc by adding 4 or 5 c.c. of ammonium hydrogen sulphite solution (made from 1:4 ammonia) to 200 c.c. of the zinc solution and boiling. If gallium is present it will be precipitated in granular form and can be filtered and washed by decantation. The precipitate is dissolved in a few drops of hydrochloric acid, diluted to 200 c.c. with water, and reprecipitated as before. This is filtered, washed, ignited, and weighed as Ga_2O_3. The potassium ferrocyanide test is sensitive to 0·0002 gram of gallium, and may be used to detect this element in the presence of zinc. If sodium or ammonium hydrogen sulphite is added to such a cold solution and then potassium ferrocyanide, there will be no precipitation, but on the addition of a few drops of hydrochloric acid the gallium will be precipitated, but not the zinc. J. F. S.

Hydrochloric Acid Colour Method for Estimating Iron. J. C. Hostetter (*J. Amer. Chem. Soc.*, 1919, **41**, 1531—1543).—A method has been elaborated by which the yellow colour produced by dissolving ferric chloride in hydrochloric acid may be used for the estimation of iron. This involves the comparison of the tint with standard tints. The temperature-coefficient for the colour varies 2—3% per degree, depending on the concentration of the iron and probably also on the acidity. The colour developed by a given amount of iron varies with the acid concentration, reaching the maximum intensity at 26—28% of hydrochloric acid. The relative increase produced by acid is greater the higher the concentration of iron; this is especially true above 20% of hydrochloric acid, but below this concentration the relative change is independent of the iron content. Inasmuch as solutions must frequently be boiled in order to ensure complete solution of the iron present as "scale," the use of constant boiling acid is recommended, and its use has been found to be altogether satisfactory. The effect of salts on the colour indicates that sulphates cause bleaching, and chlorides intensification; a detailed study of the effect of calcium chloride

shows that an intensification of 2·5 may be attained by the addition of this salt; consequently, when testing for iron in a very soluble chloride the standard iron solution must be made up to the same salt concentration. J. F. S.

A Method for the Quick Estimation of the Nickel-Iron in Meteorites. G. T. Prior (*Min. Mag.*, 1919, **18**, 349—353).—The classification of meteorites based on the amount of nickel–iron they contain and the ratio of iron to nickel in this metallic portion (A., 1916, ii, 635) requires a rapid method applicable to meteoric stones for the estimation of these quantities. The sieved material is separated into attracted and unattracted portions by a magnetic comb. The former is digested with dilute aqua regia, and the insoluble silicate which was entangled with the metal separated off; estimations of the silica and sulphur give the amounts of the soluble silicate (olivine) and the troilite (FeS); these, deducted from the weight of the attracted portion, give the weight of the nickel–iron. Nickel is estimated by precipitation with dimethylglyoxime in an aliquot portion of the solution. The method is applied to the partial analysis of seventeen meteoric stones, and the results (percentage of nickel–iron, and ratio of Fe + Co : Ni) are tabulated. L. J. S.

Electroanalysis of Nickel without Platinum Electrodes. Emilio Fernández-Espina (*Anal. Fis. Quim.*, 1919, **17**, 199—205. See A., 1916, ii, 494).—A copper cathode and a rotating iron anode, rendered passive by immersion in nitric acid, were employed. About 0·1 gram of pure nickel was dissolved in 15 drops of nitric acid and the solution evaporated to dryness after the addition of 18 drops of sulphuric acid. The various electrolytes were prepared by the further addition of the following to the nickel sulphate thus obtained: (1) sodium phosphate solution and 10 c.c. of concentrated ammonia solution; (2) 5 c.c. of 50% ammonium acetate solution and 10 c.c. of ammonia; (3) 15 c.c. of 25% formic acid and 15 c.c. of ammonia; (4) 5 grams of ammonium oxalate in 15 c.c. of water and 15 c.c. of ammonia; (5) 2 grams of crystallised boric acid and 15 c.c. of ammonia; (6) 2 grams of tartaric acid and 10 c.c. of ammonia. In each case a convenient quantity of water was also added. During the electrolysis the electrolyte was kept slightly warm, and the current increased progressively from 0·4 ampere to about 0·8 ampere. The results were moderately satisfactory in all cases except the last, in which the iron of the anode appeared to be dissolved and deposited with the nickel. W. S. M.

Estimation of Tin. F. Le Naour (*Ann. Chim. anal.*, 1919, [ii], **1**, 308—309).—The author finds that ignited stannic oxide (SnO_2) is not appreciably hygroscopic, although Bertiaux has stated the contrary (A., 1918, ii, 408). One gram of the oxide absorbed only 2 mg. of moisture when exposed to the atmosphere for eighteen hours. W. P. S.

The System *n*-Butyl Alcohol–Acetone–Water. Joseph Reilly and Edgar W. Ralph (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 597—608).—The densities of a series of *n*-butyl alcohol–acetone–

water mixtures have been determined, and graphs from these prepared with rectangular and triangular co-ordinates. From these results the composition of an unknown mixture may readily be obtained with a fair degree of accuracy if a density determination and the estimation of one constituent are made. The limit of solubility of *n*-butyl alcohol in water at 20° is 7·9% and of water in *n*-butyl alcohol 20%. The maximum contraction for mixtures of *n*-butyl alcohol and water within the range of solubility at 20° is 0·74%.

Acetone and *n*-butyl alcohol are miscible in all proportions, there being a slight increase of volume on mixing. W. G.

Estimation of Methyl Chloride in Gas Mixtures. V. C. Allison and M. H. Meighan (*J. Ind. Eng. Chem.*, 1919, **11**, 943—946).—The method proposed depends on the solubility of methyl chloride in glacial acetic acid, and is particularly useful for estimating the proportion of methyl chloride in chlorinated natural gas. A measured volume of the gas is led six times into a Hempel pipette containing glacial acetic acid, and then returned to the measuring burette; the contraction in volume gives the quantity of methyl chloride present. One volume of acetic acid absorbs more than 40 volumes of methyl chloride and 4 volumes of natural gas, but the solubility of the latter is very small when the gaseous mixture contains 40% or more of methyl chloride. The results obtained agree with those found by the partial pressure method (A., 1915, ii, 100). W. P. S.

Sulphonal. A. Falck (*Pharm. Zentr.-h.*, 1919, **60**, 409—416).—The solubility of sulphonal in various solvents was found to be as follows, the figures representing grams of solvent required to dissolve 1 gram of the substance: Water at 15°, 423; water at 100°, 8; 90% alcohol at 15°, 60; ether at 17°, 79; chloroform at 20°, 3·3; methylene chloride, 2·8; benzene at 17°, 12·7; ethyl acetate, 13·7; toluene, 19·3; carbon tetrachloride, 110; carbon disulphide, 440; 2% sodium chloride solution at 18°, 440. Owing to the fact that sulphonal begins to volatilise at 60° and is very appreciably volatile in the presence of water-vapour, solutions containing the substance should not be concentrated by evaporation before the quantity of sulphonal is estimated. The sulphonal should be extracted with chloroform and the extract evaporated at a low temperature. Sulphonal is stable for a long time in the presence of decomposing organic matter, and characteristic crystals may be obtained from its ether or chloroform solution. W. P. S.

The Estimation of the Volatile Fatty Acids by an Improved Distillation Method. Joseph Reilly and Wilfred J. Hickinbottom (*Sci. Proc. Roy. Dublin Soc.*, 1919, **15**, 513—538).—It is known that when dilute solutions of organic fatty acids are distilled certain regularities are observed. Various forms of distillation constants have been suggested by Duclaux (A., 1896, ii, 504), Naumann and Müller (A., 1901, i, 204), and Stein (A., 1913, ii, 670)

to express such regularities. These constants may be derived from Nernst's law of distribution, and on this law the authors base a discussion of the theory of distillation of dilute solutions. A method of distillation at constant volume, in which only small changes in concentration occur, is recommended, and an apparatus is described in which this process may be simply and satisfactorily carried on. The distillation constants of the fatty acids from formic to octoic have been determined, and it is shown that there is a definite relationship between the rate of distillation and the molecular constitution of these acids. Acids containing a branched carbon chain have higher constants than normal acids of the same molecular weight.

The methods of calculation are quite satisfactory for establishing the identity and purity of a solution of a single volatile fatty acid, and also give fairly accurate results in the analysis of "two-acid" mixtures. The results with mixtures of three acids are not so satisfactory. The method may be applied to fermentation products. By suitable modification of the apparatus the distillation constants for the volatile acids in butter and coco-butter can be determined and utilised for detecting the presence of adulterants. W. G.

Estimation of Lactic Acid by Oxidation. O. Schuppli (*Mitt. Lebensmittelunters. u. Hyg.*, **10**, 44—47; from *Chem. Zentr.*, 1919, ii, 894).—Szeberényi's process (A., 1918, ii, 138) gives trustworthy results in aqueous solution, but is not applicable to wines. H. W.

Naphtharesorcinolcarboxylic [1 : 3-Dihydroxynaphthalene-2-carboxylic] Acid as a Reagent for Glycuronic Acid. Y. Asahina and C. Hasegawa (*Yakugakuzasshi* [*J. Pharm. Soc. Japan*], 1919, No. 448, 484—489).—1 : 3-Dihydroxynaphthalene-2-carboxylic acid, which cannot be preserved unchanged for any length of time, is best kept in the form of the barium salt, from which it is prepared, when required, by treatment with hydrochloric acid. The authors also describe the preparation of this reagent from phenylacetic acid by Metzner's method (A., 1898, i, 152). Chemical Abstracts.

Detection of Small Amounts of Chloral in the Presence of Chloroform and Formalin Embalming Fluid. A. O. Gettler (*Proc. Soc. Exp. Biol. Med.*, 1919, **16**, 110—116; from *Physiol. Abstr.*, 1919, **4**, 255).—When kept at the ordinary temperature for half an hour with sodium carbonate and phloroglucinol, chloral develops lilac to orange, to blood orange, to deep red colorations, the shade depending on the amount of chloral present. Chloroform does not give this reaction; formaldehyde and acetaldehyde give a red colour. With resorcinol and sodium carbonate, chloral gives a red colour and a green fluorescence, the latter even in dilute solution; chloroform does not yield the green fluorescence, whilst substances of an aldehydic character do not give the reaction. H. W.

Estimation of Acetone, Methyl Alcohol, and Furfuraldehyde in the Presence of Each Other. H. Pringsheim and E. Kuhn (*Zeitsch. angew. Chem.*, 1919, **32**, 286—290).—The furfuraldehyde is precipitated by treating a portion of the mixture with phenylhydrazine in the presence of sodium acetate, the precipitate being collected, dried under reduced pressure over sulphuric acid, and weighed; its weight multiplied by 0·516 gives the corresponding quantity of furfuraldehyde. The filtrate from the phenylhydrazone precipitate is distilled with the addition of an excess of hydrochloric acid, and the distillate redistilled from magnesium oxide. In this second distillate, the methyl alcohol is estimated by oxidation with dichromate and sulphuric acid in the cold. Provided that the oxidation mixture contains about 2% of potassium dichromate (for example, 25 c.c. of distillate containing not more than 0·2 gram of methyl alcohol, 50 c.c. of *N*/1-potassium dichromate solution, and 50 c.c. of dilute sulphuric acid), the methyl alcohol is oxidised completely in eighteen hours, but the acetone is not attacked. The acetone is estimated iodometrically in a separate portion of the distillate. [See, further, *J. Soc. Chem. Ind.*, 1919, 877A.] W. P. S.

Some Iodometric Estimations. Preliminary Studies on a Micro-method for the Estimation of Acetone. Malte Ljungdahl (*Biochem. Zeitsch.*, 1919, **96**, 325—345. Compare A., 1917, ii, 584).—The author points out and discusses in detail the conditions which must be observed in the iodometric titrations employed in his micro-method for the estimation of acetone in order to ensure accuracy. S. S. Z.

A Micro-method for the Estimation of the Total Acetone in Blood. Malte Ljungdahl (*Biochem. Zeitsch.*, 1919, **96**, 345—362).—The principle of the method consists in distilling the acetone from the blood collected in a capillary tube into a solution containing an excess of iodine and alkali. The solution is then boiled in order to convert the acetone into chloroform, and the residual iodine is estimated by titrating with thiosulphate. S. S. Z.

Detection and Estimation of Traces of Hydrocyanic Acid in Complex Mixtures. L. Chelle (*Bull. Soc. Pharm., Bordeaux*, 1919, 140; from *J. Pharm. Chim.*, 1919, [vii], **20**, 156—157*).—The solution containing hydrocyanic acid or a cyanide is acidified with sulphuric acid, and air, free from carbon dioxide, is aspirated through the solution; the air is then passed through a vessel containing alkali hydroxide, which absorbs the hydrocyanic acid, and the latter is estimated subsequently by the ferrocyanide or ammoniacal silver iodide method. The whole of the hydrocyanic acid is removed from 50 c.c. of solution containing 0·48 to 54 mg. of hydrocyanic acid when the air current is maintained for three hours at the rate of 75 litres per hour. W. P. S.

* See also *Compt. rend.*, 1919, **169**, 973—975.

Detection and Estimation of Traces of Thiocyanate in Complex Mixtures. L. Chelle (*Bull. Soc. Pharm., Bordeaux*, 1919, 150; from *J. Pharm. Chim.*, 1919, [vii], **20**, 158—159 *).—The thiocyanate is oxidised to cyanide by means of potassium chromate in sulphuric acid solution; the hydrocyanic acid is then separated by passing a current of air through the solution, as described in the preceding abstract. W. P. S.

The Transformation of Hydrocyanic Acid into Thiocyanic Acid in the Course of Cadaverous Putrefactions. Experiments made in vitro. L. Chelle (*Compt. rend.*, 1919, **169**, 726—728).—From experiments with blood in vitro, the author shows that, during putrefaction, hydrocyanic acid or its salts are converted into thiocyanic acid, and that this change is very rapid. Hydrocyanic acid may be regenerated from the thiocyanic acid by oxidation with chromic acid. W. G.

Test to Distinguish between Caffeine and Theobromine. Freeman P. Stroup (*Amer. J. Pharm.*, 1919, **91**, 598—599).—A small portion of the alkaloid is spread in a thin film on a white porcelain surface, and two drops of a solution of 1 gram of potassium dichromate in 20 c.c. of concentrated sulphuric acid are placed in the centre of the film. With caffeine, the colour of the reagent almost immediately changes to bright bluish-green, whilst with theobromine the yellow colour of the reagent changes first to dark purple, then gradually to purple-green, and later to the same bluish-green tint given by caffeine. If desired, the test may be carried out in the reverse way, the alkaloid being added to two drops of the reagent, but in both cases the time required for the production of the green colour is very much less with caffeine than with theobromine. W. P. S.

Examination of Commercial Samples of Nicotine. Percival J. Fryer and C. Henry Fryer (*Analyst*, 1919, **44**, 363—369).—Commercial nicotine is sometimes adulterated with pyridine, and the presence of this substance makes it impossible to estimate the nicotine by titration or by precipitation with silicotungstic acid. The difference in the refractive indices of nicotine and pyridine, however, provides a method for the estimation. The following figures are taken from tables in the original, which show the refractive index of aqueous solutions containing 1 to 100% of either substance in differences of 1%.

If a sample contains pyridine, the percentage of nicotine calculated from the titration will be larger than the percentage calculated from the refractive index, and the difference between the percentages will give approximately the percentage of pyridine present. Another method is as follows: 25 grams of the sample are diluted with water to 100 c.c. and heated at 99° for ten minutes, cooled, and, after some hours, the refractive index of the surface liquid is determined. Under these conditions, the greater part of

* See also *Compt. rend.*, 1919, **169**, 973—975.

Nicotine. Per cent.	n_D^{15}.	Pyridine. Per cent.	n_D^{15}.
100	1·5300	100	1·5136
95	1·5255	95	1·5088
90	1·5193	90	1·5028
85	1·5118	85	1·4960
80	1·5035	80	1·4884
75	1·4950	75	1·4799
70	1·4852	70	1·4710
65	1·4743	65	1·4616
60	1·4663	60	1·4516
55	1·4523	55	1·4414
50	1·4413	50	1·4317
45	1·4303	45	1·4219
40	1·4193	40	1·4123
35	1·4083	35	1·4025
30	1·3976	30	1·3927
25	1·3868	25	1·3829
20	1·3760	20	1·3731
15	1·3652	15	1·3632
10	1·3546	10	1·3532
5	1·3443	5	1·3435
0	1·3341	0	1·3341

the nicotine separates as a heavy oil, whilst the pyridine remains in solution. In the case of pure nicotine, the refractive index obtained shows, according to the above table, 9·7% of nicotine; when pyridine is present to the extent of more than 10%, this figure is increased, and reference to the following table will give the approximate extent of the adulteration:

Pyridine. Per cent.	n_D^{15} of aqueous liquid.
0	1·3540
10	1·3558
15	1·3587
20	1·3616
25	1·3640
30	1·3662
35	1·3684
40	1·3705

The quantity of pyridine present may also be estimated by a fractional distillation method; 100 c.c. of the sample (adjusted to 95% of nicotine, as shown by the refractive index, by the addition of water or by concentration over sulphuric acid) are distilled from a standard Engler flask up to 150°. The volume of the distillate is noted (it does not exceed 5 c.c. in the case of pure nicotine), the refractive index is determined, and the percentage of pyridine found from the following table:

n_D^{15} of distillate.	Pyridine. Per cent.
1·357	0
1·366	1
1·401	5
1·436	10
1·454	15
1·467	20
1·477	25

W. P. S.

Identification and Estimation of Solanine. DEJUSSIEU (*Bull. pharm. sud-est.*, 1919, **24**, 357—361).—The method of Bellot (*Arch. Med. Pharm. milit.*, April, 1914) for the estimation of solanine in potatoes is criticised, because it involves the use of boiling water acidified with sulphuric acid in extracting the alkaloid. The author directs attention to the fact that solanine is an unstable base which is readily hydrolysed by hot dilute acids, yielding dextrose, rhamnose, galactose, and solanidine. A number of authorities are cited in support of this criticism. With reference to the identification of the alkaloid, the work of Ogier ("Traité de Toxicologie") is quoted, who states that hot dilute solutions of solanine in ethyl or amyl alcohol gelatinise on cooling, and that this property is particularly characteristic of this base.

CHEMICAL ABSTRACTS.

The Colorimetric Estimation of Hæmoglobin. BARNETT COHEN and ARTHUR H. SMITH (*J. Biol. Chem.*, 1919, **39**, 489—496).—The general technique recommended by Palmer (A., 1918, ii, 88) is employed, but the standard solution is acid hæmatin, as in the Sahli method ("Lehrbuch Klin. Untersuch. Methoden," 1909, 845). The hæmoglobin of whole blood is converted into acid hæmatin with hydrochloric acid and compared with a standard in a colorimeter of the Autenreith-Hellige pattern. An acid hæmatin standard, prepared from the blood of one species, may be used in the colorimetric estimation of hæmoglobin in the blood of a variety of other species. J. C. D.

Technique of Chemical Blood Analysis. II. A Comparison between Macro- and Micro-methods. M. RICHTER-QUITTNER (*Biochem. Zeitsch.*, 1919, **96**, 92—106).—A critical comparison against macro-methods of some well-known micro-methods employed in blood analysis. The conclusion arrived at is that, with some modifications, these methods are capable of giving accurate results. S. S. Z.

Analysis of Gastric Juice. CERBELAUD (*Union pharm.*, 1918; from *Ann. Chim. anal.*, 1919, [ii], **1**, 299—301).—The acidity is estimated by titration with $N/10$-sodium hydroxide solution, using phenolphthalein as indicator. The total chlorine is estimated by treating 5 c.c. of the gastric juice with 2 c.c. of sodium hydroxide solution (D 1·332) and 2 c.c. of 5% potassium permanganate solution; 10 c.c. of concentrated nitric acid are then added, the mixture, after fifteen minutes, is diluted with 50 c.c. of water, and the chlorine titrated with silver nitrate and thiocyanate solutions. Organic chlorine and fixed chlorine are estimated together in the same way after the gastric juice has been evaporated to dryness, and the residue heated at 100° for one hour. Fixed (mineral) chlorine is titrated in the ash obtained by evaporating the gastric juice and incinerating the dry residue at a low temperature; in this case, the treatment with alkaline permanganate and nitric acid is also employed. W. P. S.

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ERRATA.

Vol. XCII (Abstr., 1907).

Page	Line	
i. 216	bottom	*for* "m.p. 240°" *read* "m.p. 204°."

Vol. CIV (Abstr., 1913).

Page	Col.	Line	
i. 780		17	*for* "Nitrous oxide" *read* "Nitric oxide."
		19	
		20	
		10*	
		9*	
		4*	
ii. 1210	i.	32	
		36	
ii. 1337		28	
ii. 1390	ii.	19*	

Vol. CVIII (Abstr., 1915).

Page	Col.	Line	
i. 326		18	*for* "Nitrous oxide" *read* "Nitric oxide."
		21	
ii. 934	ii.	16	
ii. 1079		8–10	the entry "behaviour of various substances with (Panzer), A., i, 326," should be transposed to line 19 (under nitrogen dioxide).

Vol. CXVI. (Abstr., 1919).

Page	Line	
i. 357	15	*for* "antipyrine" *read* "1-phenyl-3-methyl-5-pyrazolone."
i. 402	1	,, "Brener" *read* "Breuer."
i. 559	13	,, "Eric Doddrell Evans" *read* "Eric Doddrell Evens."
ii. 261	13	,, "ten" *read* "two."
ii. 263	24	,, "Albert Noyes" *read* "William A. Noyes, jun."
ii. 312	20	,, "Kirchof" *read* "Kirchhof."
ii. 327	7*	,, "Langhaus" *read* "Langhans."
ii. 351	15	,, "Zepfel" *read* "Zipfel."
ii. 443	3*	,, "Horsh" *read* "Horsch."
ii. 446	7*	*after* "421·73°" *insert* "on the platinum resistance scale.'
ii. 529	15*	*for* "chloroform" *read* "iodoform."

* From bottom.

INSTRUCTIONS TO ABSTRACTORS,

GIVING THE

NOMENCLATURE AND SYSTEM OF NOTATION

ADOPTED IN THE ABSTRACTS.

THE object of the abstracts of chemical papers published elsewhere than in the Transactions of the Society is to furnish the Fellows with a concise account of the progress of chemical science from month to month. It must be understood that as the abstracts are prepared for the information of the Fellows in general, they cannot possibly be made so full or so detailed as to obviate on the part of those who are engaged on special investigations the necessity of consulting the original memoirs.

1. Titles of papers must be given literally.
2. Before beginning to write the abstract, the whole of the original paper must be read, in order that a judgment may be formed of its importance and of the scale on which the abstract should be made.
3. In the case of papers dealing with subjects not strictly chemical, the abstract should refer only to matters of chemical interest in the original.
4. The abstract should consist mainly of the expression, in the abstractor's own words, of the substance of the paper.
5. The abstract should be made as short as is consistent with a clear and accurate statement of the author's results.
6. A concise statement showing the general trend of the investigation should be given at the commencement of those abstracts where the nature of the original permits of it.
7. If an abstract of a paper on the same subject, either by the author of the paper abstracted, or by some other author, has already appeared, note should, as a rule, be made of this fact.
8. Matter which has appeared once in the *Abstracts* is not to be abstracted again, a reference being given to the volume in which the abstract may be found.
9. As a rule, details of methods of preparation or analysis, or generally speaking of work, are to be omitted, unless such details are essential to the understanding of the results, or have some independent value. Further, comparatively unimportant compounds, such as the inorganic salts of organic bases or acids, should be mentioned quite shortly. On the other hand, data such as melting and boiling points, sp. gr., specific rotation, &c., must be given in every case unless recorded in earlier papers.

Nomenclature.

10. Employ names such as *sodium chloride, potassium sulphate* for inorganic compounds, and use the terminals *ous* and *ic* only in distinguishing compounds of different orders derived from the same elementary radicle; such, for instance, as mercurous and mercuric chlorides, sulphurous and sulphuric acids.

11. Term compounds of metallic radicles with the OH-group *hydroxides* and not hydrates, the name hydrate being reserved for compounds supposed to contain water of combination or crystallisation.

12. Term salts containing an amount of metal equivalent to the displaceable hydrogen of the acid, *normal* and not neutral salts, and assign names such as sodium hydrogen sulphate, disodium hydrogen phosphate, &c., to the acid salts. Basic salts as a rule are best designated merely by their *formulae*.

13. Names in common use for oxides should be employed, for example: NO, nitric oxide; CO_2, carbon dioxide; P_4O_{10}, phosphoric oxide; As_4O_6, arsenious oxide; Fe_2O_3, ferric oxide.

14. In open chain compounds, Greek letters must be used to indicate the position of a substituent, the letter α being assigned to the first carbon atom in the formula, except in the case of CN and CO_2H, for example, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CH_2I$ α-iodobutane, $CH_3 \cdot CH_2 \cdot CH_2 \cdot CN$ α-cyanopropane.

15. Isomeric open chain compounds are most conveniently represented as substitution derivatives of the longest carbon chain in the formula; for example,

$$CH_3 \cdot CH_2 \diagup\!\!\diagdown CH \cdot CH \diagup\!\!\diagdown \begin{matrix} CH_3 \\ CH_3 \end{matrix}$$ or $CH_3 \cdot CH_2 \cdot CHMe \cdot CHMe \cdot CH_3$

should be termed $\beta\gamma$-dimethylpentane not methylethyl*iso*propylmethane, and $\begin{matrix} CH_3 \\ CH_3 \end{matrix} \diagup\!\!\diagdown CH \cdot CH \diagup\!\!\diagdown \begin{matrix} CH_3 \\ CO_2H \end{matrix}$ or $CH_3 \cdot CHMe \cdot CHMe \cdot CO_2H$

should be termed $\alpha\beta$-dimethylbutyric acid, not $\alpha\beta\beta$-trimethylpropionic, or α-methyl*iso*valeric, or methyl*iso*propylacetic acid.

16. Use names such as methane, ethane, &c., for the normal paraffins or hydrocarbons of the C_nH_{2n+2} series of the form $CH_3 \cdot [CH_2]_5 \cdot CH_3$, &c. Term the hydrocarbons C_2H_4 and C_2H_2 ethylene and acetylene respectively (not ethene and ethine). Homologues of the ethylene series are to be indicated by the suffix *-ene*, and those of the acetylene series, wherever possible, by *-inene*. Adopt the name allene for the hydrocarbon $CH_2{:}C{:}CH_2$.

17. Distinguish all hydroxyl derivatives of hydrocarbons by names ending in *ol*. Alcohols should be spoken of as mono-, di-, tri-, or n-hydric, according to the number of OH-groups. Compounds which are not alcohols, but for which names ending in *ol* have been used, are to be represented by names ending in *ole*, if a systematic name cannot be given, thus anisole not anisol, indole not indol. Compounds such as MeONa, EtONa, &c., should be termed sodium methoxide, sodium ethoxide, &c.

18. The radicles indicated in the name of a compound are to be

given in the order fluoro-, chloro-, bromo-, iodo-, nitro-, nitroso-, amino-, imino-, cyano-, thiocyano-, hydroxy-, keto-.

19. Compounds analogous to the acids of the lactic series containing the OH-group should be termed *hydroxy*-derivatives, and not oxy-derivatives; for example, hydroxyacetic and not oxyacetic acid. Compounds containing the analogous groups OEt, OPh, OAc, &c., should in like manner be termed ethoxy-, phenoxy-, acetoxy- derivatives. Thus α-ethoxypropionic acid, $OEt{\cdot}CHMe{\cdot}CO_2H$, instead of ethyl-lactic acid; 3:4-diethoxybenzoic acid, $(OEt)_2C_6H_3{\cdot}CO_2H$, instead of diethylprotocatechuic acid; and α-acetoxypropionic acid, $OAc{\cdot}CHMe{\cdot}CO_2H$, instead of acetyl-lactic acid. Terms such as diethylprotocatechuic acid should be understood to mean a compound formed by the displacement of hydrogen atoms in the hydrocarbon radicle of protocatechuic acid by ethyl, thus, $C_6HEt_2(OH)_2{\cdot}CO_2H$, and not $C_6H_3(OEt)_2{\cdot}CO_2H$, just as dibromoprotocatechuic acid is understood to be the name of a compound of the formula $C_6HBr_2(OH)_2{\cdot}CO_2H$.

20. The term *ether* should be restricted to the oxides of hydrocarbon radicles and their derivatives, and the esters (so-called compound ethers or ethereal salts) should be represented by names similar to those given to metallic salts.

21. When a substituent is one of the groups NH_2, NHR, NR_2, NH or NR, its name should end in *ino*; for example, β-aminopropionic acid, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$, β-anilino-acrylic acid, $NHPh{\cdot}CH{:}CH{\cdot}CO_2H$, α-iminopropionic acid, $NH{:}CMe{\cdot}CO_2H$.

22. Compounds of the radicle SO_3H should, whenever possible, be termed sulphonic acids, or failing this, sulpho-compounds; for example, benzenesulphonic acid, sulphobenzoic acid.

23. Basic substances should invariably be indicated by names ending in *ine*, as aniline instead of anilin, the termination *in* being restricted to certain neutral compounds, viz., glycerides, glucosides, bitter principles, and proteins, such as palmitin, amygdalin, albumin. The compounds of basic substances with hydrogen chloride, bromide or iodide should always receive names ending in *ide* and not *ate*, as morphine hydrochloride and not morphine hydrochlorate.

24. The Collective Index, 4th decade (1903–1912) should be adopted as the standard of reference on questions of nomenclature not provided for in the preceding sections.

Notation.

25. In empirical formulae the elements are to be given in the order C, H, O, N, Cl, Br, I, F, S, P, and the remainder alphabetically.

26. Equations should be omitted unless essential to the understanding of the results; as a rule, they should not be written on a separate line, but should "run on" with the text.

27. To economise space, it is desirable:

(a) That *dots* should be used instead of *dashes* in connecting contiguous symbols or radicles, whenever this does not interfere with the clearness of the formula.

(b) That formulae should be shortened by the judicious employment of the symbols Me for CH_3, Et for C_2H_5, Pr^{α} for $CH_2{\cdot}CH_2{\cdot}CH_3$, Pr^{β} for $CH(CH_3)_2$, Ph for C_6H_5, Py for C_5H_4N, Ac for $CO{\cdot}CH_3$, and Bz for $CO{\cdot}C_6H_5$.

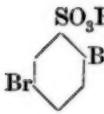
(c) That formulae should be written *in one line* whenever this can be done without obscuring their meaning.

28. In representing the constitution of benzene derivatives, the relative positions of the radicles in the symbol of benzene should be indicated by numerals, instead of by means of the hexagon formula.

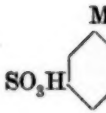
(a) The abbreviations *o*-, *m*-, and *p*-, should be used in place of 1 : 2- or ortho-, 1 : 3- or meta-, and 1 : 4- or para.

(b) In numbering positions in the case of substitution derivatives of phenol, aniline, benzonitrile, benzoic acid, benzenesulphonic acid, benzaldehyde, and toluene, the characteristic radicle of each of these parent substances is to be regarded as in position 1 (compare Collective Index).

(c) Names of substitution derivatives should be given in such a way that the position of the substituent is indicated by a numeral prefixed; for example :—



Br is 2 : 5-dibromobenzenesulphonic acid;



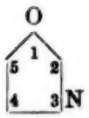
3-bromo-*o*-toluidine-5 sulphonic acid.

29. In representing the constitution of derivatives of other "closed chain" hydrocarbons, graphic formulae should not be employed, but the system of numbering positions indicated in Richter's *Lexikon der Kohlenstoff-Verbindungen* (3rd edition, 1910, pp. 14—26) should be used, of which the following schemes may be regarded as typical :—

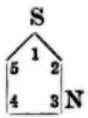
Furan.

Thiophen.

Pyrrole.

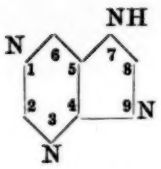


Oxazole.



Thiazole.

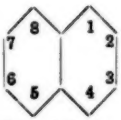
Pyrazole.



Purine.*

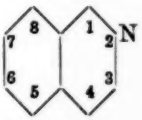
Pyridine.

Indole.

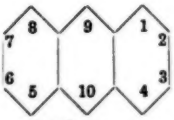


Naphthalene.

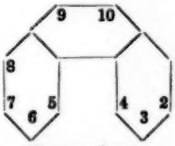
Quinoline.



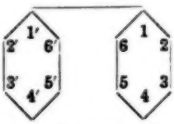
*iso*Quinoline.



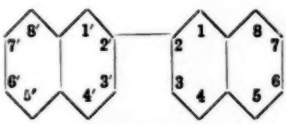
Anthracene.



Phenanthrene.



Diphenyl.



ββ-Dinaphthyl.

Manuscript.

30. In view of the difficulty of dealing with MSS. of widely varying sizes, abstracts cannot be accepted unless written on quarto paper (10 × 8 in.).

31. Not more than one abstract must appear on a sheet.

32. When an abstract exceeds a sheet in length, the sheets must be fastened together by means of gum at the top left-hand corner.

33. The name of the abstractor must be written diagonally at the top left-hand corner of the first sheet of the abstract.

Proofs.

34. Abstractors are expected to read and correct proofs carefully, and to check all formulae and figures against MSS.

35. All proofs, however small, must be returned to the Sub-Editor not later than 24 hours after receipt from the printers.

***** The Editor's decision, in all matters connected with the Abstracts, must be considered final.**

* This numbering, proposed originally by E. Fischer, is adopted in the text of the *Lexikon*.